Spontaneous Resolution through Helical Assembly of a Conformationally Chiral Molecule with an Unusual Zwitterionic Structure

S. Jayanty and T. P. Radhakrishnan*[a]

Abstract: A conformationally chiral zwitterionic molecule forms mutually orthogonal helical superstructures in the crystal. This is achieved through a network of hydrogen bond pathways, and electrostatic interactions in crystals formed with and without water of crystallization. A systematic protocol for the computation of charge distribution on the 'molecule-in-the-crystal' is presented; the computed charges provide an insight into the origin of the intermolecular electrostatic interactions. The coexisting orthogonal helical formations lead to the homochiral assembly, and spontaneous resolution observed in the crystals. This material facilitates an appraisal of the molecular level interactions, which form the basis for the persistent spontaneous resolution of a conformationally chiral molecule in the solid state.

Keywords: conformational chirality · helical structures · hydrogen bonds · spontaneous resolution

Introduction

Molecular assembly in crystals is directed by the concomitant influence of a variety of intermolecular interactions. The resulting organization in the crystal along with the molecular characteristics determine the attributes of the materials. Among the various molecular superstructures that exert critical control on the materials properties, helical organization is one of the most fascinating, for reasons of symmetry, and the cooperativity of extended interactions associated with such structures. The inherent chirality of helical structures is of considerable interest in the design of liquid crystals,[1] and quadratic nonlinear optical materials for applications such as second harmonic generation.[2,3] A wide variety of intermolecular interactions have been harnessed to build helical molecular assemblies. Hydrogen bonding is the method of choice in many cases.[4] There are a number of helical coordination polymers, in which the metal–ligand interactions, and the chirality of the ligand or the coordination geometry is effectively exploited.[5] We have reported on the formation of helical superstructures of axially chiral push-pull molecules achieved through dipolar nitro group interactions.[3] The helicity of the extended structures, in most of these cases, stems directly from the chirality, often axial C_2 symmetry, of the building blocks. Polyisocyanides and polyheteroarenes are interesting cases, in which steric factors drive the formation of the helical structure of the polymer backbone.[6]

Another context in which helical assembly assumes fundamental significance is when it is accompanied by spontaneous resolution in crystals. Spontaneous resolution has important implications for areas such as chirality in nature,[7] enantioselective synthesis,[8] and advanced materials design.[9] Fundamental thermodynamic aspects of spontaneous generation of optical activity have been discussed previously.[10] The intimate relation between chirality and crystals,[11] and spontaneous resolution in supramolecular architectures[12] have been reviewed recently. Since little is known about the factors that govern conglomerate formation, it is of great interest to examine the formation of helical assemblies that trigger such events, and the molecular level structure and interactions, which lead to such chiral supramolecular associations. Molecules which are chiral, not due to the presence of a stereogenic atom, but because of a specific conformational structure that lacks all improper rotation symmetries, and the enantiomeric forms of which can be interconverted through rotation about a single bond, could be called conformationally chiral.[13] Conformationally chiral compounds which resolve spontaneously in the crystalline state (1,1′-binaphthyl is a classic example)[14] are particularly significant, since the barriers to racemization in such molecules are relatively low, and therefore the con-

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. This describes the mechanism for the formation of DPODQ and provides details of the crystal structures of BDPDQI, DPODQ·H_2O and DPODQ, and the summary of semiempirical computations on the dication of BDPDQI and DPODQ.

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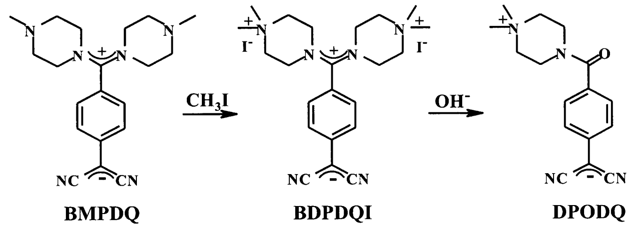
glomerate formation through supramolecular assembly is a particularly subtle phenomenon.

We have been investigating diaminodicyanoquinodimethanes (DADQ), because of their quadratic nonlinear optical applications,[15,16] and more recently due to the enhanced solid state fluorescence exhibited by some of the derivatives (eg., BMPDQ in Scheme 1).[17] We have now observed spontaneous resolution through helical organization in crystals of a related molecule decorated with a variety of ionic and potential hydrogen bonding sites. 7-(*N*,*N*-dimethylpiperazinium)-7-oxo-8,8-dicyanoquinodimethane (DPODQ) (Scheme 1) possesses cyano groups, an amide group, and a quarternary ammonium functionality capable of participating in hydrogen bonds (O–H···N and C–H···O) or electrostatic interactions. Charge distribution estimated by using a systematic protocol based on semiempirical computations suggests an unusual zwitterionic structure with the negative charge residing on the dicyanomethylene end of the conjugated π-electron system, and a compensating positive charge on the nonconjugated remote[17,18] ammonium functionality. The molecule is conformationally chiral owing to the strong molecular twist between the amide group and the benzenoid ring plane, a feature similar to that found in the precursor DADQ molecules, as well[15–18]; there are no stereogenic atoms on the molecule. In this paper, we present the structures of DPODQ crystals with and without water of crystallization, both of which reveal helical superstructure motifs along the three crystallographic directions through a combination of electrostatic interactions and hydrogen bonds. The concomitant formation of the helical structures expresses the homochirality of the molecular assembly, which leads to the spontaneous resolution in these crystals. The circular dichroism (CD) and second harmonic generation (SHG) of the microcrystalline material are reported.



Scheme 1. Synthesis of DPODQ.

Results and Discussion

The diiodide salt of 7,7-bis(*N*,*N*-dimethylpiperazinium)-8,8-dicyanoquinodimethane (BDPDQI), (Scheme 1) shows the unusual enhancement of fluorescence in the solid state, similar to its precursor molecule we recently investigated.[17] Crystal structure analysis showed that BDPDQI possesses a centrosymmetric lattice belonging to the monoclinic $P2_1/c$ space group with one molecule in the asymmetric unit. The molecular structure is shown in Figure 1 (left), and the crystallographic details are given in Table 1. As in other DADQ's, BDPDQI exhibits a zwitterionic structure, which is reflected in the nearly benzenoid geometry of the aromatic ring, and the short C7–N9, C7–N10 bond lengths

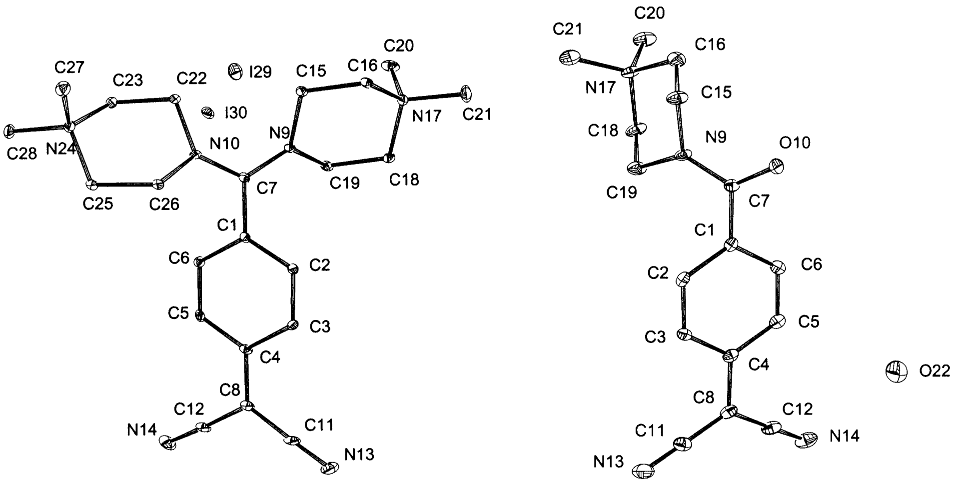


Figure 1. Molecular structure of BDPDQI (left) and DPODQ•H$_2$O (right) from single crystal X-ray analysis; 10% probability thermal ellipsoids are shown; hydrogen atoms are not shown.

Table 1. Crystallographic data[19] for BDPDQI, DPODQ·H$_2$O and DPODQ.

	BDPDQI	DPODQ·H$_2$O	DPODQ
formula	$C_{22}H_{32}N_6I_2$	$C_{16}H_{20}N_4O_2$	$C_{16}H_{18}N_4O$
M_r	634.34	300.36	282.34
crystal system	Monoclinic	Orthorhombic	Orthorhombic
space group	$P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)	$P2_12_12_1$(No. 19)
a [Å]	13.0471(14)	10.064(4)	10.5556(17)
b [Å]	16.2113(18)	11.40(2)	10.645(6)
c [Å]	13.0823(16)	14.047(9)	13.0717(15)
β [°]	111.207(9)	90	90
V [Å^3]	2579.7(5)	1612(4)	1468.8(9)
Z	4	4	4
ρ_{calcd} [g cm^{-3}]	1.633	1.237	1.277
μ [cm^{-1}]	24.58	0.84	0.83
T [K]	293(2)	293(2)	293(2)
λ [Å]	0.71073	0.71073	0.71073
observed reflections	3486 [$I \geq 2\sigma(I)$]	1582 [$I \geq \sigma(I)$]	1927 [$I \geq \sigma(I)$]
parameters	271	211	196
GOF	0.806	0.937	1.054
R [$I \geq 2\sigma(I)$]	0.0282	0.0583	0.0472
wR^2[$I \geq 2\sigma(I)$]	0.0905	0.1736	0.1063

(Table 2); this implies partial double bond character, and stabilization of the positive charge on the diaminomethylene moiety. We have previously defined the quinonoid–benzenoid character (QBC) in terms of the deviations of the bond lengths in the six membered ring from an ideal value of 1.400 Å, such that the latter has a QBC value of 1.000.[20] The QBC value of BDPDQI is found to be 0.724. The charge separation between the diaminomethylene unit (positive), and the dicyanomethylene substituted benzenoid ring (negative) is facilitated by the strong molecular twist of 49.3° (average of the dihedral angles N9-C7-C1-C2 = 49.0°, and N10-C7-C1-C6 = 49.6°), a common feature of the DADQ's, as noted above.

Table 2. Significant bond lengths (A: C1–C7; B: average of C1–C2 and C1–C6, C: average of C2–C3 and C5–C6, D: average of C3–C4 and C4–C5, E: C4–C8, F = average of C7–N9 and C7–N10 for BDPDQI and C7–N9 for DPODQ, G = C7–O10 for DPODQ) in Å, and twist angle θ in degrees, in the dication part of BDPDQI and DPODQ from X-ray structure analysis (the latter in DPODQ•H_2O), and from AM1 and AM1/COSMO ($\varepsilon = 20$) computations (see Figure 1 for atom labeling).

	BDPDQI (Å [°])			DPODQ (Å [°])		
Parameter	X-ray	AM1	AM1/COSMO	X-ray	AM1	AM1/COSMO
A	1.477	1.381	1.474	1.489	1.438	1.479
B	1.396	1.456	1.408	1.395	1.418	1.402
C	1.372	1.349	1.380	1.382	1.369	1.387
D	1.414	1.454	1.419	1.391	1.434	1.414
E	1.450	1.365	1.416	1.489	1.392	1.425
F	1.338	1.431	1.369	1.337	1.461	1.392
G	–	–	–	1.241	1.253	1.260
θ	49.3	1.6	50.4	49.5	15.8	45.4

Semiempirical AM1[21] calculations, which incorporate the solvation subroutine COSMO[22] are quite successful in modeling the twisted structure of DADQ's as they exist in the crystal lattice: the so called 'molecule-in-a-crystal'.[23] AM1/COSMO computations involving full geometry optimization with an imposed dielectric constant (ε) of 20 or higher, reproduced quite well, the molecular structure of the BDPDQI dication in the solid state; Table 2 lists significant geometry parameters computed at $\varepsilon = 20$. The inadequacy of AM1 alone is also demonstrated. The geometry optimization provides an estimate of the ε that may be employed to mimic the molecular environment in the crystal. We have computed the atomic charge distribution on this dication by the AM1/COSMO method; the molecular structure from the crystal analysis was used with hydrogen atom positions alone optimized. When the ε values employed in the computation are low, the computed charge distribution varies strongly with the ε. However, a consistent charge distribution is obtained at higher values of ε, typically at ≥ 20. Based on the geometry optimization above, the values obtained at $\varepsilon = 20$ are expected to be realistic estimates for the crystal state, and are schematically represented in Figure 2 (left). The zwitterionic nature of the π-electron system is revealed by the negative charge on the dicyanomethylene group (the group charge is −0.80), and the positive charge at the diaminomethylene end (the group charge including the the carbons connected to the nitrogen atoms is +0.90). Nearly a full positive charge each is seen on the quarternary ammonium moieties (the charge resides almost exclusively on the methylene and methyl groups connected to the nitrogen); more details may be found in the Supporting Information.

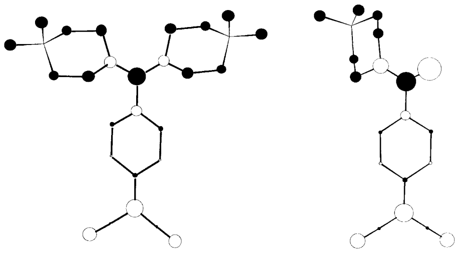


Figure 2. AM1/COSMO ($\varepsilon = 20$) computed charge distribution in the dication part of BDPDQI (left) and DPODQ (right); filled and open circles indicate positive and negative charges respectively, and the radius is proportional to the net charge on an atom and any hydrogen atoms connected to it.

When we attempted the substitution of the iodide ions in BDPDQI by organic ions through reactions with the corresponding salts in aqueous medium, it was found that instead of anion substitution, one of the piperazinium units was displaced and replaced by an oxygen atom. This rather unexpected reaction can be easily rationalized and achieved by a directed approach by simply dissolving BDPDQI in an aqueous solution of KOH (Scheme 1). The DPODQ formation is likely to involve the attack of OH^- on the diaminomethylene carbon followed by the expulsion of a piperazine (see Supporting Information). DPODQ was crystallized from water–methanol. Chemical characterization and crystal structure analysis showed that no counterion is present, hence there is no net charge on DPODQ. More significantly, the crystal is found to belong to the chiral space group, $P2_12_12_1$ with one molecule in the asymmetric unit; a molecule of water is also included (Figure 1, Table 1). The molecular structure again shows a strong twist of 49.5° (average of the dihedral angles N9-C7-C1-C2 = 50.6° and O10-C7-C1-C6 = 48.4°). The benzenoid ring bond lengths are more symmetric than in BDPDQI; this is reflected in the higher QBC value of 0.844. AM1/COSMO computations again show that the structure is modeled quite well at $\varepsilon \geq 20$ (Table 2). The charge distribution computed at $\varepsilon = 20$ for the molecular structure from crystal analysis is schematically represented in Figure 2 (right). It suggests an unusual zwitterionic structure, which consists of a net negative charge on the dicyanomethylene moiety (the group charge is −0.89), and a positive charge on the nonconjugated quarternary ammonium group (the group charge is +0.91). Furthermore, the amide moiety shows strong charge polarization. The charge distribution is thus quite asymmetric, and different from that in BDPDQI. This appears to play a key role in evolving the very different molecular assembly described below.

DADQ's with their ground state molecular twist are chiral structures, C_2 symmetric when the amino functionalities are identical. However, like BDPDQI, so far all of them have formed achiral crystal lattices, except those in which stereogenic centers were incorporated.[15,24] DPODQ presents a new situation with lower molecular symmetry (C_1), and the consequent asymmetric charge distribution. Furthermore, the molecule possesses well-exposed charge sites and hydrogen bond functionalities which can enter into strong intermolecular interactions. The crystal structure reveals short intermolecular contacts between the amide oxygen atom, and the quarternary ammonium group; the closest C···O distances are 3.231 (C20···O10), and 3.390 Å (C21···O10); the resulting N17···O10 distance is 3.580 Å. These intermolecular contacts indicate appreciable C–H···O and electrostatic interactions, which in turn lead to the formation of an extended structure along the crystallographic *b* axis. The molecular organization may be viewed as a 2_1 chain, however, two piperazinium–carbonyl [N17(C15,C16,C18,C19)N9-C7-O10] moieties connected in succession can be visualized as forming one turn of an extended helical superstructure (Figure 3a). The view along the packing axis clarifies the sense of helicity as left-handed (*M*). DPODQ·H_2O exhibits also extended hydrogen bond interactions between the cyano groups and the water molecule of crystallization; the relevant distances (angles) are, $r_{O22\cdots N13} = 3.017$ Å ($\theta_{O22\text{-}H22B\cdots N13} = 149.16°$), and $r_{O22\cdots N14} = 3.038$ Å ($\theta_{O22\text{-}H22A\cdots N14} = 157.31°$). These lead to the formation of the 2_1 chain along the crystallographic *c* axis. Once again, a helical motif (Figure 3b) can be visualized with two water–dicyanomethylene units in succession, which form one turn; the view along the packing axis shows the sense of helicity to be right-handed (*P*). The two 2_1 symmetric superstructures along the orthogonal crystallographic directions is accompanied by a 2_1 symmetric structure along the third direction, which leads to the $2_12_12_1$ symmetry of the crystal space group. The *M*-helical molecular assembly formed along the *a* axis can be visualized as arising from a combination of the electrostatic interactions and hydrogen bonds (Figure 4).

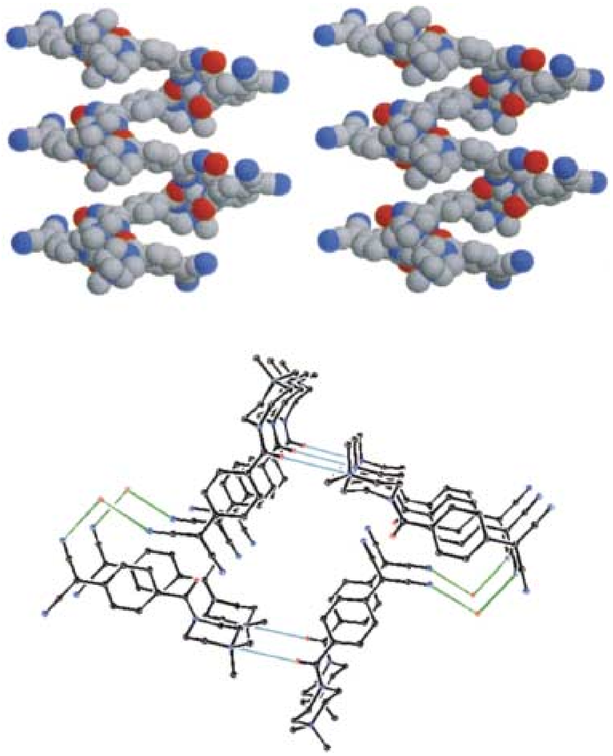


Figure 4. *M*-helical assembly of DPODQ molecules in DPODQ·H_2O crystal along the *a* axis; the intermolecular interactions shown in Figure 3a (cyan) and b (green) are indicated. Top; stereo view perpendicular to the helical axis (space filling model); C (grey), N (blue), and O (red) atoms are indicated, and bottom; view along the helical axis; C (black), N (blue), and O (red) atoms are indicated.

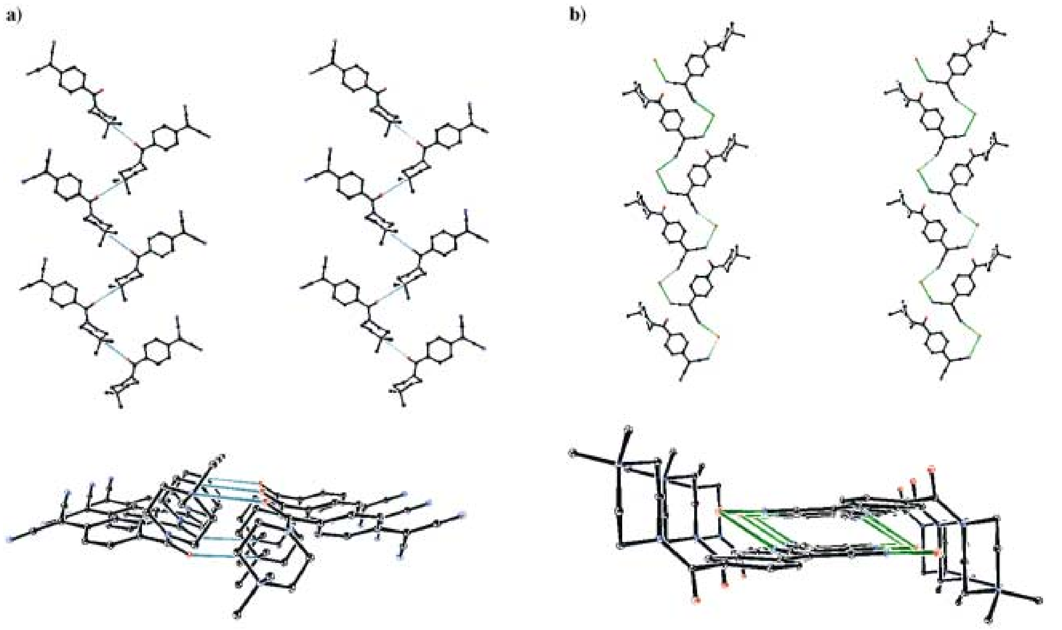


Figure 3. a) *M*-helical motif in DPODQ·H_2O crystal along the *b* axis; the intermolecular interactions (cyan) are indicated between O10 and N17 for easier viewing and b) *P*-helical motif in DPODQ·H_2O crystal along the *c* axis; the hydrogen bonds (green) are indicated. Top; stereo view perpendicular to the helical axis, and bottom; view along the helical axis; C (black), N (blue) and O (red) atoms are indicated.

Interestingly, crystals of DPODQ grown from concentrated water–methanol solutions showed a slightly different unit cell. Structural investigation showed that this crystal does not contain the water molecule; however, it belongs to $P2_12_12_1$ space group with one molecule in the asymmetric unit with a molecular structure nearly identical to the one before. The crystallographic data are provided in Table 1. The significant observation in this crystal is that, once again, helical assemblies are formed along each of the crystallographic directions. Since O−H···N bonding option does not exist now, all intermolecular contacts are based on C−H···O or electrostatic interactions, and the considerably short distances indicate that these are likely to be strong. The supramolecular assemblies along the crystallographic *a*, *b*, and *c* axes are formed through the C20···O10 (3.279 Å), C18···O10 (3.069 Å), and C7···N14 (3.261 Å) contacts, respectively (Figure 5). Once again, the molecular organizations are 2_1 chains; helical motifs are formed along the *a* and *b* axes through successively connected piperazinium–carbonyl moieties, and along the *c* axis through the zwitterion links. The crystal structures of DPODQ with and without water molecules of crystallization provide a dramatic demonstration of the persistent tendency of this molecule towards helical organization!

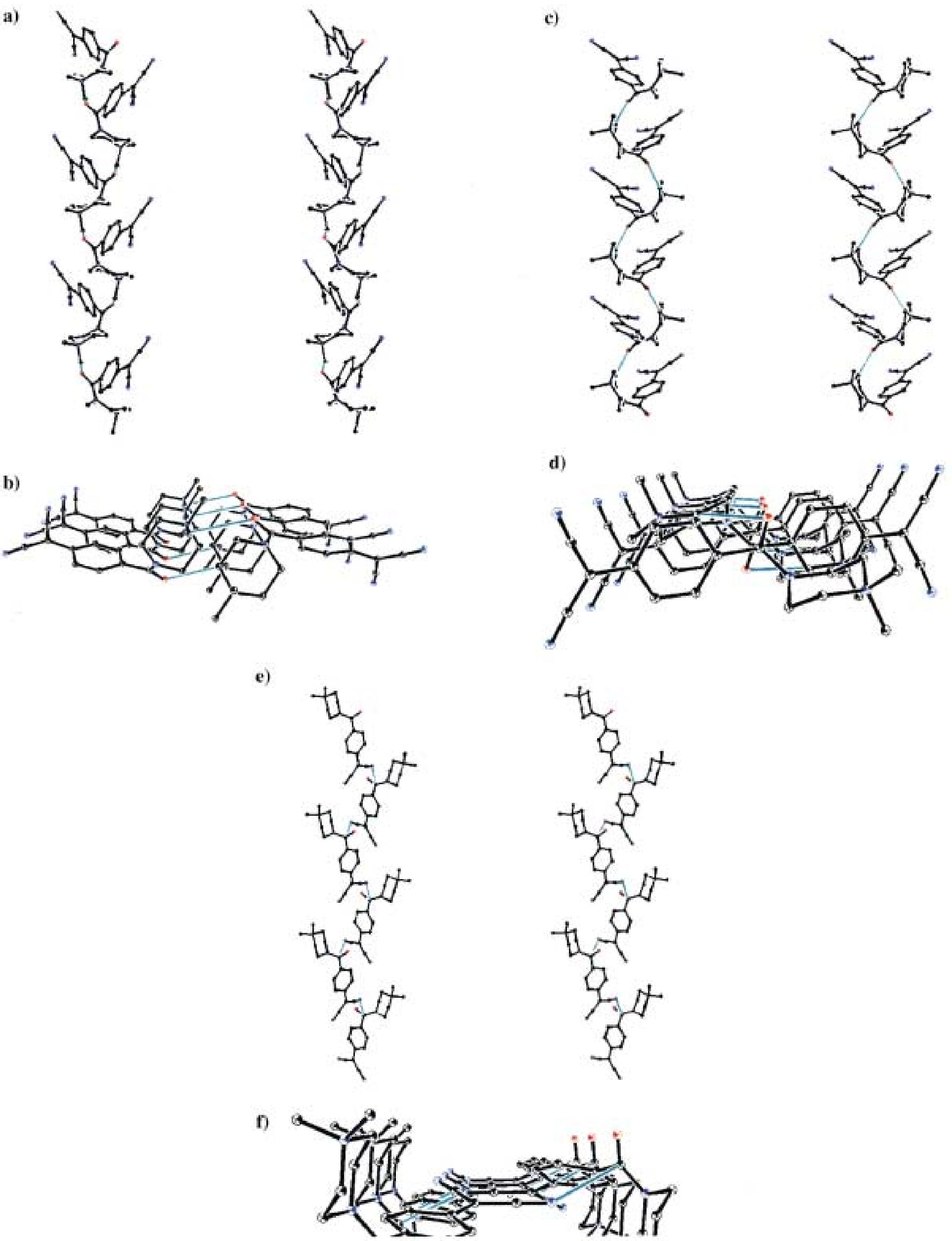


Figure 5. *M*-helical motifs in DPODQ crystal along the a) and b) *a*, c) and d) *b*, and e) and f) *c* axes; the hydrogen bond and electrostatic interactions (cyan) are indicated. Top; Stereo view perpendicular to the helical axis, and bottom; view along the helical axis; C (black), N (blue), and O (red) atoms are indicated.

Several cases of spontaneous resolution of achiral molecules through hydrogen bonded assemblies are known.[12,25] Spontaneous resolution has also been achieved through cocrystallization.[26] In the case of DPODQ crystals, single component helical superstructures are formed from conformationally chiral zwitterionic molecules through electrostatic and hydrogen bond interactions. The inherent homochirality of the orthogonal helical assemblies lays the basis for the spontaneous resolution. Crystals of DPODQ show high melting points close to 300 °C, possibly a result of the extended lattice structure built through multiple noncovalent interactions, which include strong electrostatic ones. Since large crystals could not be grown, we have attempted to measure the CD of small single crystals by grinding with KBr, and forming solid pellets. As reported earlier,[27] considerable optimization of conditions was required. After several attempts with many crystals, we were able to obtain spectra showing a negative CD. Figure 6 shows the CD spectrum along with the absorption profile; the molar ellipticity is calculated as reported in Ref. [27]. In spite of extensive efforts, the spectrum of the enantiomorphous crystal, which shows positive CD has proved elusive so far. AM1/TDHF[28] computation indicates that DPODQ has an appreciable first order hyperpolarizability, and the static β is calculated to be 51.9 esu. Therefore, the noncentrosymmetric material is expected to show SHG in the solid state. Kurtz–Perry measurements[29] on microcrystalline samples show a moderate value of two to three times that of urea.

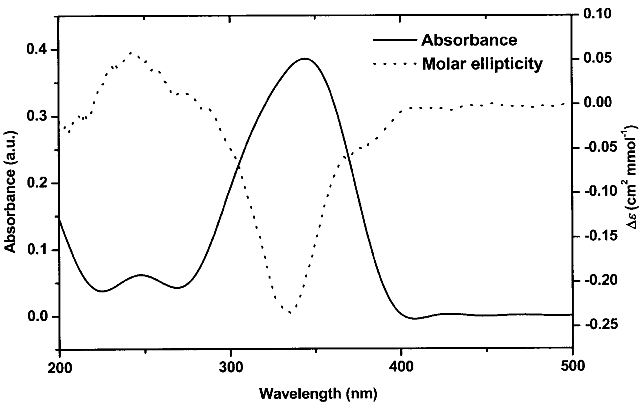


Figure 6. The electronic absorption and circular dichroism spectra of DPODQ•H_2O single crystal ground with KBr and fabricated in the form of pellet.

Conclusion

DPODQ is a conformationally chiral molecule with an unusual zwitterionic structure. Semiempirical computational modeling of the molecule-in-the-crystal reveals the presence of enhanced charges on several atoms, which together with the hydrogen bond functionalities present on the molecule, lead to strong intermolecular interactions. The low symmetry of the twisted molecule coupled with the extended non-covalent interactions lead to the formation of helical superstructures along orthogonal crystallographic directions. The homochirality associated with the orthogonal helical assemblies leads to the spontaneous resolution in the crystalline state. This molecule should serve as a prototype to guide novel strategies that exploit a wide spectrum of molecular level interactions to achieve chiral supramolecular assembly.

Experimental and Computational Methods

The syntheses followed Scheme 1. The procedure for the synthesis of BDPDQI and DPODQ, and their characterizations are given below.

Diiodide salt of 7,7-bis(*N*,*N*-dimethylpiperazinium)-8,8-dicyanoquinodimethane (BDPDQI): 7,7-Bis(*N*-methylpiperazino)-8,8-dicyanoquinodimethane (BMPDQ) was prepared as reported earlier.[17] Freshly distilled methyl iodide (1.03 g, 7.22 mmol) was added to BMPDQ (0.25 g, 0.71 mmol) in acetonitrile (30 mL). The solution changed from yellow to deep orange. It was then stirred at 25 °C for 30 min, and a yellow microcrystalline product separated out. Stirring was continued for seven more hours to ensure the completion of the reaction. The precipitate was filtered, washed, and dried (0.37 g, 82 %) to give yellow BDPDQI. It was recrystallized from water. M.p.=270–275 °C (decomp); FTIR (KBr): $\tilde{\nu}$= 2993.0, 2173.9, 2135.4, 1597.2, 1460.2 cm^{-1}; UV/Vis (acetonitrile): λ_{max} = 462.5, 355.0, 247.5 nm; elemental analysis (%) calcd for $C_{22}H_{32}N_6I_2$: C 41.77, H 5.06, N 13.30; found C 41.54, H 5.01, N 13.35.

7-(*N*,*N*-Dimethylpiperazinium)-7-oxo-8,8-dicyanoquinodimethane hydrate (DPODQ•H_2O): A solution of KOH (0.04 g, 0.71 mmol) in water (2 mL) was added to a solution of BDPDQI (0.30 g, 0.47 mmol) in water (30 mL). A pale yellow microcrystalline product of DPODQ immediately formed, and was filtered, washed, and dried (0.102 g, 77 %). It was recrystallized from water–methanol (1:1). M.p.=295–300 °C (decomp); FTIR (KBr): $\tilde{\nu}$=3476.0, 3034.3, 2166.3, 2123.8, 1628.1 (C=O stretch), 1599.1, 1419.7 cm^{-1}; UV/Vis (acetonitrile) : λ_{max} =355.0, 224.0 nm; ^1H NMR ([D$_6$]DMSO): δ=3.3–3.4 (s, 6H), 3.4–3.5 (t, 4H), 3.8–3.9 (t, 4H), 6.7–6.8 (d, 2H), 7.2–7.3 ppm (d, 2H); ^{13}C NMR ([D$_6$]DMSO) : δ=7.3, 30.2, 50.8, 60.5, 117.4, 121.6, 125.1, 128.8, 145.3, 170.4 ppm; elemental analysis (%) calcd for $C_{16}H_{18}N_4O.H_2O$: C 64.00, H 6.66, N 18.66; found: C 63.75, H 6.68, N 18.85. Slow (~24 h) crystallization from dilute solutions (~0.01 M) gave DPODQ•H_2O, while faster (~6 h) crystallization from more concentrated solutions (~0.02 M) yielded DPODQ (m.p.=285–290 °C).

Crystal structure determination: X-ray diffraction data were collected on an Enraf-Nonius MACH3 diffractometer. $Mo_{K\alpha}$ radiation with a graphite crystal monochromator in the incident beam was used. Data was reduced by using Xtal3.4;[30] Lorentz and polarization corrections were included. Empirical absorption correction was applied in the case of BDPDQI by using ψ-scan data. All non-hydrogen atoms were found by means of direct method analysis in SHELX-97,[31] and refined anisotropically. After several cycles of refinement, the positions of the hydrogen atoms were calculated and added to the refinement process; hydrogen atom positions were refined for the water molecule alone in DPODQ•H_2O, imposing constraints of O–H (1.00(3) Å), and H–H (1.62(6) Å) distances. The Flack parameter was refined in the case of the DPODQ crystal, and gave a value of 0.085(0.007). Details of data collection, solution and refinement, fractional coordinates with anisotropic thermal parameters, and full lists of bond lengths and angles are submitted as Supporting Information.

Electronic spectroscopy: Samples were made from crystalline DPODQ (0.1–0.2 mg microcrystals for the reflectance and 0.5–1.5 mg single crystal for the CD spectra) ground with KBr (80–100 mg) in an agate mortar, and pressed into pellets by using a pressure of ~10 ton in a standard press. The pellets were 0.5–0.6 mm thick. The specular reflectance (8° incidence) spectra were recorded on a Shimadzu UV-visible Spectrometer (Model UV-3101) by using the integrating sphere (ISR 3100) attachment; the reflectance spectra were converted to the absorption profiles by using the Kubelka–Munk function. The circular dichroism spectra were recorded on a Jasco Spectropolarimeter (Model J-810) employing a band width of 2 nm. The spectra were smoothed by using standard smoothing functions.

Semiempirical computations: Semiempirical quantum chemical calculations were carried out by using the AM1 method in the MOPAC93 program package.[21] The microenvironment of the molecule in the crystal was simulated by using the solvation model COSMO;[22] the parameter, NSPA (number of segments per atom) was set equal to 60 in all calculations. EF (eigen vector following) method, and PRECISE conditions were employed in all optimizations. Calculations were carried out on fully optimized geometries, and on the molecular geometry from crystal structure with hydrogen atom positions alone optimized. Detailed results are provided in the Supporting Information.

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