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On the Nature of Non-Covalent Interactions in isomers of 2, 5-Dichloro-1,4-Benzoquinone dimers – Ground- and Excited-State Properties

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Abstract

The competition between non-covalent interactions (NCIs) such as C-H---O, C-H---Cl, C-Cl---O, C-Cl---Cl-C, C-O---C, C-Cl---C and C-O---π in the isomers of 2, 5-dichloro-1,4-benzoquinone (DCBQ) dimer were investigated by quantum chemical calculations to study the properties of ground and excited states. All the interactions were identified through bond critical points (BCP) at Atoms In Molecule (AIM) study. Isomer 1 (I_H) and isomer 6 (I_P) were surprisingly very stable; the largest stabilization energies of 4.16, 5.39 kcal/mol respectively were observed for ground state and 5.67, 6.07 kcal/mol respectively were observed for excited state at the MP2/6-31++G (d, p) level of theory. The orientations of the excited-state isomers were similar to the ground-state except for isomer 5 (I_X) and isomer 9 (I_M), which disturbed the relative energy stability order. The calculated absorption spectra have shown two absorption splits for isomers 5, 7, 8 and 9 through the acute angle between the transition dipole moment of the monomers. The circular dichroism (CD) couplet of the CD spectrum and the value of optical rotation (OR) have indicated that isomers 1, 3, 5, 7, 8 and 9 have chiral characteristics. The study of the absorption and CD spectra has revealed the impact of intermolecular NCIs in chirality.

Key words: DCBQ molecule, Atoms in molecule, excited state, absorption spectrum, CD spectrum, chirality.

Introduction

Intermolecular non-covalent interactions (NCIs) such as hydrogen bonds, halogen bonds, π---π stacking and X---H/π interactions play an important role for molecular orientation, assembly, stability in the crystal structure, the dynamical properties of biological molecules, and chemical reactions[1, 2]. For the past several decades, scientists have been trying to explain NCIs and their role for the above process through well-defined quantum chemical concepts, but the study of NCIs continues to be a challenging problem in science. Hydrogen bonding is a ubiquitous electrostatic NCI that is stabilized by electrostatic dipole interaction, dispersion and charge transfer between acceptor and donor atoms. The energy of a hydrogen bond cannot be described by any single type of energy, since it comprises electrostatic interaction, electron delocalization, exchange repulsion, and dispersion energy [3-5].

Large number of experimental [6-8] and theoretical studies [9-12] have focused not only on the hydrogen bond but also on the halogen bond. Material scientists have been interested in studying the stability of supramolecular behavior in order to fine-tune the properties of X-ray crystals using crystal engineering. A halogen bond is an σ-hole bond i.e. it is an interaction between two electronegative atoms where polarizable halogens exhibit electrophilic (δ^+) character (a small amount of the positive region) along the axis of the C-X bond. Hence, halogen bonding is an interaction between the charge depletion zone (σ-hole) in the valence shell of a halogen atom and the charge concentration of an electron-rich system Y. It also has its own nucleophilic (δ^-) character perpendicular to the C-X bond. Halogen atoms have both electrophilic and nucleophilic characters when covalently bonded with another, in particular carbon atom [13-17]. In addition, a dihalogen bond is described by the positive potential of a halogen atom interacting with the negative sites on another halogen atom (the halogens can be identical or different)[18]. Nowadays chalcogen[19], pnicogen[20] and tetral or carbon bonds[21] have drawn their attention through large number of theoretical studies[22]. These are described in a similar way as halogen bonds, through the presence of VI, V, IV groups of atoms. C-O/N--- π bond is one of the types of intermolecular NCIs, where the partial negative charges of the lone-pair atom interact with the π orbital in the positive region. An electron-withdrawing group of an atom or functional group removes electron density from a conjugated π system via resonance or inductive electron withdrawal, thus making the π system more electrophilic. An electron-donating group has of reducing electrophilicity. It is a rare interaction in a natural material[23].

The above-described features and phenomena mainly depend on the corresponding positive and negative regions responsible for the formation of NCIs. Three types of interactions are noticeable in the arrangement of crystal structure: 1) The interaction between partially negative and partially positive charges or σ-hole occurring due to polarizability (e.g. hydrogen and halogen bonds between Lewis acid–base pairs), 2) the interaction between a negative region (created by resonance) which is at the π-orbital due to resonance (e.g. C---H/π and O---H/π interactions) and partially positive charges or σ-hole, 3) the interaction between a partially negative charge and the positive region (created by resonance) which is also at the π-orbital due to resonance (e.g. C---O/π interactions). Among these three types, the first one is the most important NCI for all the fields. In the past several decades, numerous studies have been devoted to a comparison of the properties and features of the first two types, but the third one has received less attention among scientists.

The physical and chemical properties of non-covalent bonded systems in the ground state have been widely studied experimentally[6, 24, 25] and theoretically[26-28] in the last decades. Recently, Row et al.[23] have studied experimentally the various kinds of NCIs occurring in the crystal structure of 2,5-dichloro-1,4-benzoquinone (DCBQ) (which is reported in the

Cambridge crystal data centre ,CCDC number : 807801) and analyzed the charge density of the structure using the quantum chemical method. The crystal structure of 2,5-dichloro-1,4-benzoquinone (DCBQ) were considered for the present study. . Destro et al.[6] have studied the C=O···C=O, C−H···O, Cl···O and Cl···Cl interactions in the crystal structure of 2, 6-dichloro-p-benzoquinone using both experimental and theoretical methods. The experimental and theoretical studies[29-33] have reported the importance of the role of an excited-state hydrogen bond in many photo-physical processes and photochemical reactions. Upon the electronic excitation of the non-covalent bonded systems by light, the donor and acceptor molecules reorganize themselves in the electronic excited state due to the significant charge-distribution difference between different electronic states. Further, the experimental study[34] has reported the changes in the absorption spectrum with respect to hydrogen and halogen bonds. This paves the way for the analysis of the ground- and excited-state properties of DCBQ having a set of isomers formed through a different NCI with a cooperativity effect. The impact of hydrogen bonding in the exciton coupling phenomena has been reported by Pescitelli et al.[35, 36]. Moreover, chiral distinction or "chiral recognition" has been a topic of interest for both theoreticians and experimentalists. Hence the understanding of the non-covalent interactions involving chirality arrangement will help us to understand the behavior of hydrogen, halogen and carbon bonding in the excited state.

The properties of the intermolecular NCIs existing in the crystal structure of DCBQ were analyzed and compared both in ground and excited states. The different types of the NCIs in DCBQ such as hydrogen bonds (C-H…O, C-H…Cl), halogen bonds (C-Cl…O), (C-Cl…Cl-C) and other interactions (C-O…C, C-Cl…C and C-O… π) occurring due to the presence of two polarized chlorines, two polarized oxygens and two polarized hydrogens will be discussed in detail. Insight into the nature of the stabilization of these systems is obtained by performing quantum mechanical calculations (QM). The QM calculations describe hydrogen, halogen bonding, π interactions and their characteristics in a straightforward way, unlike molecular mechanics, which fails[37]. Furthermore, the relative energy, interaction energy and Localized Molecular Orbital Energy decomposition analysis (LMOEDA) have been carried out to understand the nature of the interaction within the isomers. The similarity between the total interaction energy and dispersion energy does not necessarily mean that the second energy is dominant. This will happen also in the case when attractive electrostatic energy and repulsive exchange–repulsion energy compensate[37]. Exciton coupling is analyzed to understand the close proximity, orientation, the impact of NCI in the optical rotation (OR) value and the Circular dichroic (CD) spectrum, which are strictly allied to chirality. Altogether nine different isomers of the DCBQ dimer, which cover all the NCIs were analyzed and compared not only in the ground state but also in the excited state to have an in-depth knowledge of the properties of NCIs.

Computational Details

Hohenstein et al.[38] have reported significant improvement of M05-2X, a DFT functional for NCI calculations. Many theoretical investigations [39-42] have confirmed that the TD-DFT method is a useful tool for the study of electronically excited states. Geometry optimizations for the ground and the lowest singlet excited states of the DCBQ monomer and its nine dimer isomers were performed using the density functional theory (DFT) and time-dependent density functional theory methods (TD-DFT) at the M05-2X/6-31++G (d, p) level of theory. In order to have a more rigorous energy comparison, an MP2/6-31++G (d, p) single-point energy calculation was performed at the ground state for M05-2X geometries. All the optimized model structures correspond to the minima in the potential energy surface since imaginary frequencies were not observed. Here the shift calculation was interpreted for all parameters through the relation $\Delta A = A$ (complex)-A (monomer).

The interaction energies for all the isomers at the ground state were calculated after applying the basis set superposition error (BSSE) using the counterpoise calculation $\Delta E(A,B) = E(A,B) - \{E(A) + E(B)\}$ at the MP2/6-31++G (d, p) and M05-2X /6-31++G (d, p) levels of theory. In addition, interaction energies without counterpoise correction for all the isomers at the excited state were calculated at M05-2X/6-31++G (d, p) level of theory using the above-mentioned formula. An interesting tool for the study of the nature of NCIs is localized molecular orbital energy decomposition analysis (LMOEDA),[43] in which the energy is decomposed into terms of electrostatic (ES), polarization (PL), exchange-repulsion (EX), dispersion (DISP) and repulsion (REP) energies. The LMOEDA has been carried out to calculate the interaction energies at the MP2/ 6-311G** level of theory using the GAMESS software[44].

Interactions of monomer electronic excited states lead to a quantum delocalization of electronic excitation (exciton). This delocalization affects the absorption and circular dichroism (CD) spectra, which lead to the fluorescent resonant energy transfer (FRET) between different monomers or isomers[45-47]. The exciton-split CD spectrum (a CD couplet) consists of two Cotton effects of the opposite signs explained by the "exciton chirality method", which originates in the spatial interaction between two or more strong chromophoric electric dipole transitions that are chirally arranged and close in energy. Absorption and CD spectra were calculated using the gaussSum-2.2.5 program with the full width at half maximum (FWHM) being 3000/cm for the absorption spectrum and the σ value being 0.2ev for the CD spectrum. All the computations in the present study were performed using the Gaussian 09W program[48].

The electrostatic potential map has been generated for the DCBQ monomer in order to gain insight into the nature and directionality of the dihalogen- and halogen-bond interactions being considered here. The electrostatic potentials have been computed on molecular surfaces, with a surface being defined as the 0.001 au (electrons/bohr3) outer contour of the electron density, as proposed by Bader et al. The most positive value of the potentials (maxima value) is referred to as $V_{s,max}$. There may be several of each on a given molecular surface. Here electrostatic potentials were computed at the M05-2X/6-31++G (d,p) level of theory.

Ground-State Properties

Monomer

Fig. 1a and 1b shows the electrostatic potential (ESP) of the DCBQ monomer with different views. From the figures, chlorine and carbon atom have the σ-hole at the cusp point with $V_{s,max}$ value amounting to 0.3142. Oxygen atom has negative region at the cusp point with $V_{s,min}$ value amounting to -0.0174. The centre of the molecule is observed to have a positive region, which is stabilized by resonance through a carbon atom bonded with the lone pair of oxygen and chlorine atoms.

Complexes

ESP map clearly describes the presence of all non covalent interactions except dihalogen bond indicating the absence of σ- hole for dihalogen bonds. The ESP for all isomers were drawn with $V_{s,max}$ and $V_{s,min}$ value amounting to 0.3142 and -0.0174 respectively, which are shown in Fig. 2 with different views in order to visualize clearly all the non-covalent interactions. Presence of all intermolecular non covalent interactions was conformed in Fig. 3 through bond critical point including dihalogen bonds. In hydrogen bonded isomers, positive region of hydrogen interact with negative region of oxygen upon complex formation. Whereas the negative region was decreased due to charge transfer from the acceptor to donor atom which are clearly depicted in Fig. 2 (1b, 2b, 7a, 8a). For a halogen bond interaction, negative region of the oxygen atom remains the same. The Fig. 2 (4, 5a, 8) depicts the σ- hole of chlorine atom. For a carbon bonded interaction, ESP map show the interaction between positive sites of carbon to negative site of oxygen atom.

Nine isomers of the DCBQ dimer were optimized at the M05-2X/6-31++G (d, p) level of theory. Their geometrical structures and parameters were given in Fig. S1 and Table S1, respectively, monomer parameters were given in Table S2 as supplementary material. Isomers 1, 2 and 3 are hydrogen-bonded isomers (I_H), isomers 4 and 5 are halogen-bonded isomers (I_X), isomer 6 is the carbon bonded isomer (I_c), and isomers 7, 8 and 9 are mixed isomers (I_M). Their relative-energy diagram is shown in Fig. 4. The orientation of each isomer differs only through intermolecular NCIs and it is stabilized by more than one NCI. In the case of isomers 1, 2, 3, 4, 6 and 8, each monomer acts as a donor and acceptor to another monomer for the corresponding NCI. In the case of isomers 5 and 9, monomer 1 acts as a donor and monomer 2 as an acceptor of the respective NCI. Notably for isomer 7, monomer 1 is an acceptor of the hydrogen bond and donor of the halogen bond and vice versa for monomer 2.

The LMOEDA has been used to calculate the interaction energies at the MP2/ 6-311G** level of theory; the distribution of the energy components in various isomers is shown in Fig. 5 and Table 1. The interaction energy (the sum of all the components) obtained by LMOEDA is found to be comparable with the BSSE-corrected interaction energies at the MP2/6-311++G (2d, 2p) and M05-2X/6-311++G (2d, 2p) levels of theory (Table 1). The sum of the contributions from EX and ES interactions is comparable with the REP interaction. The percentage graph in Fig. 5 has been plotted by taking into account the attractive contributions of ES, EX, PL and DISP energies. It is clear that ES and EX energies play a dominant role in the total interaction energy, where the sum of their contributions is up to 65–86%. Yet the DISP energy plays the key role in the stabilization of these motifs, contributing by 3–27%, whereas the PL contribution is 5–10 %.

Hydrogen-Bonded Isomers (I_H)

Among nine different isomers, 1, 2 and 3 are hydrogen-bonded isomers, where isomer 1, having two strong symmetric hydrogen bonds (C6-H8...O16 and C18-H20...O4), has a large stabilization energy (3.79 kcal/mol) with a low dispersion energy (-0.6 kcal/mol). The very large stabilization energy for the above isomer implies that the sum of the ES, EX and REP terms is attractive (-1.61 kcal/mol) with a comparable polarization energy of -1.59 kcal/mol. Isomer 2, having two hydrogen bonds with the oxygen acceptor C6-H8---O16 (2.29Å, 170.55^0) and chlorine acceptor C18-H20---Cl11 (3.06Å, 157.48^0), is observed to have a comparable stabilization energy (2.16 kcal/mol). The dispersion (-0.91 kcal/mol) and polarization energies (-0.92 kcal/mol) are equal and the sum of ES, EX and REP contributions is attractive (-0.33 kcal/mol). Isomer 3, having two symmetric hydrogen bonds C-H---Cl (2.96Å, 176^0) in a planar arrangement, has very weak stabilization (0.87 kcal/mol) and polarization energies (-0.36 kcal/mol). A very large dispersion energy of -1.48 kcal/mol (even larger than interaction energy) for the above isomer implies that the sum of ES, EX and REP interactions in hydrogen bonds is repulsive (0.96 kcal/mol) and that all the attraction comes from dispersion energy (-1.48 kcal/mol)[37].

Among all the hydrogen-bonded isomers, isomer 1 is the most stable with two strong hydrogen bonds. The hydrogen-bond lengths (2.29Å, 2.29Å) and angles (163.84^0, $163. 84^0$) of isomer 1 are found to be the same, because it is a symmetric hydrogen bond of the resonance-assisted hydrogen bond (RAHB) type with an oxygen acceptor. A resonance cyclic structure was formed through a hydrogen bond between the monomers. The most stable nature of isomer 1 can be explained by its favorable geometrical arrangement. The only attractive electrostatic interaction typical of a hydrogen bond could exist in isomer 1, having two strong hydrogen bonds with C-H...O bond lengths (2.29 Å) and angles (163.84°), which are close to the ideal hydrogen-bond values. Furthermore, isomer 2 with its strong hydrogen bond C6-H8...O16 (2.29 Å, 170.5°) is also close to the ideal hydrogen-bond length and angle. Nevertheless, some stabilization comes also from the weak hydrogen bond (C18-H20...Cl11; 3.0Å, 157.48 $^{\circ}$), which is far from being the ideal hydrogen-bond length and angle. The hydrogen-bond angle (176.48^{0}) of isomer 3 is strong and close to the ideal angle, but the short hydrogen-bond length (2.9Å) makes isomer 3 the least stable. Since isomer 3 is electrostatically repulsive, the stabilization of these complexes should originate in dispersion energy[37]. This was confirmed earlier with the total stabilization energy and the different contribution obtained from LMOEDA.

Halogen-bonded isomers (I_X)

The halogen-bonded isomers are isomers 4 and 5, with isomer 4 having two non-symmetric halogen bonds, C19-Cl21---O12 (3.12Å, 166.18^{0}) and C22-Cl23---O4 (3.38Å, 159.06^{0}), and one dihalogen bond C1-Cl12---Cl23 (3.62Å and 109.61^{0}) with small stabilization energy (1.22kcal/mol) and large dispersion energy (-1.61 kcal/mol). This is also caused by the fact that the sum of ES, EX and REP is repulsive (0.98 kcal/mol) and all the attractive nature comes from dispersion contribution. Surprisingly enough, the halogen bond C22-Cl23---O4 (159.06^{0}) and the dihalogen bond C1-Cl12---Cl23 (109.61^{0}) are not typical halogen bonds with the ideal angle. Here the polarization contribution is also lower (-0.59 kcal/mol). In the dihalogen bond, the cusp point of one chlorine atom interacts with the belt point of another chlorine atom. Isomer 5, having the halogen bond C1-Cl12---O21 (3.0Å,

173^0) and the dihalogen bond C1-Cl12---Cl23-C22 (3.84Å and 93^0, 138^0), has been observed to have lower stabilization energy (1.02 kcal/mol), with comparable dispersion energy (-1.31 kcal/mol) and lower polarization energy (-0.47 kcal/mol). The halogen bonds C1-Cl12---O21 and C1-Cl12---Cl23-C22 have been observed to have the ideal bond lengths and angles. The sum of ES, EX and REP, however, is electrostatically repulsive (0.75 kcal/mol), indicating that a large part of the attraction energy comes from dispersion as similar to reference [38].

Concerning isomers 4 and 5, isomer 4 is more stable with three halogen bonds than isomer 5 with two halogen bonds. The halogen-bonded isomers are less stable when compared to hydrogen-bonded isomers. Since the sum of ES, EX, REP is repulsive (ES, EX, REP) for halogen-bonded isomers, all the attractive nature comes from dispersion energy. On the other hand, the sum of ES, EX and REP is attractive for the most stable hydrogen-bonded isomers (1, 2).

Carbon bonds (I_c)

Isomer 6, having 4 carbon bonds forms two symmetric C-O---C (2.95Å, 93.44^0) and C-Cl---C (3.60Å, 96.48^0) interactions with a slightly deviated stacking arrangement resulting in larger stabilization and dispersion energies (3.77, -4.59 kcal/mol). The larger stabilization energy for the above isomer could only be explained on the basis of the geometrical arrangement of isomer 6, which allows the formation of two symmetric interactions. The two stacking interactions with distances of 2.9 and 3.5 Å are clearly the reason for the stronger stabilization of isomer 6. Indeed, the attraction here comes from dispersion, where the sum of ES, EX and REP is repulsive (2.67 kcal/mol) with a lower polarization energy of -1.86 kcal/mol.

Mixed isomers (I_M)

The mixed isomers consist of isomer 7 with hydrogen and halogen bonds; isomer 8 with π interaction and a halogen bond, isomer 9 with a hydrogen bond and a Cl...C interaction. Isomer 7, formed by the bifurcated-donor hydrogen bonds C18-H20---O4 (2.38Å, 158.86^0) and C18-H20---Cl12 (2.97Å, 133.77^0) and one halogen bond C1-Cl12---O16 (3.19Å, 151.04^0), has stabilization energy (2.46 kcal/mol) with very less dispersion (-1.42 kcal/mol) and polarization energy (-1.02 kcal/mol). Here the sum of ES, EX and REP is negligible, indicating that the attraction and repulsion energies neutralize each other. The stabilization energy is balanced by polarization and dispersion contributions. The hydrogen- and halogen-bond angles are not close to the ideal angle due to bifurcated-donor hydrogen bonds. This results in weaker stabilization energy than in other isomers.

Isomer 8, having the T-shape interaction C19-O21---π (2.91Å, 165.30^0) and the halogen-bonding interaction C22-Cl23…O4 (3.51Å, 128.17^0), has large stabilization energy (3.6 kcal/mol) with comparable dispersion energy (-3.48 kcal/mol). The sum of ES, EX and REP is repulsive (1.43 kcal/mol) and the polarization energy is -1.59 kcal/mol. The stability of isomer 8 arises from the T-shape interaction with the ideal angle (165.30^0) and distance (2.91Å). This is because of the lone-pair oxygen atom (O4) interacting with the positive region, which is stabilized by resonance through the electron-withdrawing atom bonded to the carbon atom. Isomer 9, having one hydrogen bond, C18-H20---O4 (2.29Å, 153.71^0), and one carbon bond (C22-Cl23---C2) interaction (3.50Å, 104.54^0), has the stabilization energy (2.53 kcal/mol) comparable to the dispersion energy (-2.6 kcal/mol) and less polarization energy (-1.14 kcal/mol). This is a surprising result, where the dispersion contribution and not the sum of ES, EX and REP contributions included in LMOEDA interaction energy is similar to that of interaction energy. The hydrogen bond does not correspond to a typical hydrogen bond with attractive electrostatic energy between an electron donor and hydrogen or between H20 and O4. Here the sum of ES, EX and REP is clearly repulsive (1.21 kcal/mol).

A comparison of NCIs in isomers

Among all the interactions observed, C-Cl---C is found to be the weakest among other interactions. Based on the positive and negative regions, C-H---O, C-H---Cl, C-Cl---O, C-Cl---Cl-C, C-O---C, C-Cl---C and C-O---π interactions exist in isomers. The bond length of NCIs for all nine isomers are ordered as H---O < H---Cl < O---π < O---C < Cl---O < Cl---C < Cl---Cl. This reveals that the hydrogen bond is found to be comparatively stronger than other interactions. The relative energy plot yields the order of stability for the NCIs in all isomers as Cl---Cl < Cl---C < H---Cl < Cl---O < H---O < O---π < O---C interactions. The bond distances for non covalent interactions from the experiment are Cl---Cl = 3.72Å, Cl---C = 3.70 Å, H---Cl = 2.94Å, Cl---O = 3.06Å, H---O = 2.44Å, O---π = 3.04Å, O---C = 3.09Å, which is comparable to our computational theoretical results. In addition, Hirshfeld surface analysis reported in the crystal structure[18] indeed describes the dominant order as Cl---Cl < O---π < Cl---C < O---C < H---O < H---Cl < Cl---O. Among the isomers, the relative energy stability order for isomer groups is as follows: $I_c > I_H > I_M > I_X$. Hydrogen-bonded isomers (I_H) 1, 2 and the carbon bonded isomer (I_c) 6 are the most stable with a favorable geometrical arrangement. The relative energy stability order for the isomers is as follows 6 < 7 < 8 < 1 < 9 < 2 < 4 < 5 < 3. The AIM analysis performed for the electron density q(r), laplacian of electron density $\nabla^2 q(r)$ and energy $E_{(BCP)}$ for the corresponding BCP describing the strength of the NCI have been compared and are shown in Table 2. Based on the q(r) values, the strength of NCI have been arranged as Cl---Cl < Cl---C < H---Cl < Cl---O < O---C < O---π < H---O. Correlation between electron density and laplacian of electron density for all interactions is a linear relationship with R=0.96 and is given in Fig S2. To describe the interaction energy with the energy of the BCP, interaction energies of the nine isomers are correlated with sum of energy of the BCPs for corresponding isomer as negative linear with R= -0.98 which is shown in Fig 6.

The relative energy plot in Fig. 4 shows a slight difference in the energies of isomers 6 and 7, but for the isomers the energy sharply descends as 8, 1, 9, 2, 4, 5 and 3. The Cl---O halogen bond, characterized by the sharply descending one is found to be weaker than the H---O hydrogen bond and stronger than the H---Cl hydrogen bond. According to a relative-energy diagram, isomers 6 (I_c) and 8 (I_M), which have O---C and O---π bonds, are found to be more stable than the hydrogen (I_H) and halogen (I_X) bonded isomers. Consequently, the chain arrangement of the hydrogen- and halogen-bonded isomers is also more stable. The H---O and H---Cl hydrogen bond lengths are 2.29–2.38Å, 2.95–3.0Å and 3.00–3.85Å respectively.

The vibrational frequency analysis has been performed for hydrogen, halogen and carbon bonds. The elongation of donor bond is associated with decrease in frequency and contraction of donor bond is associated with increase in frequency. These are elucidated in Table S3 as a supplementary material. The Frequency shift for hydrogen bond is more when compare with halogen bond. Symmetric hydrogen bonds of isomer 1 have the highest frequency shift value (-31.33 cm^{-1}) which is the most stabilized isomer of I_H. Non symmetric hydrogen bonds of isomer 3 have the blue shift (17.58cm^{-1}) which is the least stable isomer compare to all nine isomers. Isomer 2 has two different hydrogen bonds with oxygen acceptor (C6-H8---O16) and chlorine acceptor (C18-H20---Cl11) where oxygen acceptor hydrogen bond has high frequency shift value (-27.62cm^{-1}) compare with the chlorine acceptor hydrogen bond (-18.89cm^{-1}). All halogen bond interactions are associated with the blue shift. A symmetric halogen bond of isomer 4 has the highest frequency shift value (12.32cm^{-1}) which is more stabilized structure of I_X. C22-Cl23---O4 halogen bonds of isomer

5 has less frequency shift (2.95cm^{-1}) value. The Range of red shift value for hydrogen bond is from -16 to - 32cm^{-1} and blue shift value for halogen bond is from 3 to 13cm^{-1}. The blue shift for carbon bond is 1.05cm^{-1} for isomer 6 which is one of the most stable isomer among the nine isomers.

Excited-state properties

The geometrical structures of all the isomers were optimized using the TD-DFT method in the excited state S1, and is shown in Fig. 4, which reveals that the relative energies observed for the excited state are not similar to those of the ground-state energies. Indeed, the NCI lengths are found to differ for both of the states that are shown in Table 3. The structural changes observed in hydrogen-bonded (I_H), halogen-bonded (I_X), mixed isomers (I_M) and the carbon bonded (I_c) isomers are compared to the ground state, which will be discussed below.

Hydrogen-bonded isomers (I_H)

The orientation of the hydrogen-bonded isomers 1, 2 and 3 is similar to that of the ground state. Isomer 1 has symmetric hydrogen bonds with the oxygen acceptor (C18-H20---O4 and C6-H8---O16), which are shortened in the excited state from 0.0002 to 0.096Å with a large stabilization energy of 5.67 kcal/mol. A favorable geometrical arrangement with the ideal hydrogen-bond length (2.29, 2.20Å) and angles (163.84^0, 163.88^0) observed for isomer 1 result in a more stable nature. Isomer 2, having non-symmetric hydrogen bonds (C6-H8---O16 and C18-H20---Cl11) is shortened in the excited state up to 0.049Å. The hydrogen-bond lengths and angles are observed to have 3.03Å and 2.24Å, 163.180 and 179.61^0 respectively near the ideal values. But the stabilization energy (3.31kcal/mol) is comparatively lower. On the other hand, isomer 3, which forms a symmetric hydrogen bond with the chlorine acceptor (H8---Cl23 and H20---Cl11), is lengthened in the excited state (from 0.02 to 0.004Å). This isomer has low stabilization energy (1.78kcal/mol) when compared to all the other isomers in the excited state, but this energy is higher than ground-state stabilization energy by 0.97kcal/mol. Among all the hydrogen-bonded isomers, isomer 1 with an oxygen acceptor alone is found to be more stable than the other isomers with chlorine and oxygen acceptors.

Halogen-bonded isomers (I_X)

The orientation of the halogen-bonded isomers 4 and 5 remains the same as that of the ground state. Isomer 4 has the halogen bonds C19-Cl21---O12 and C22-Cl23---O4 (3.00Å, 3.42 Å, 169.45^0, 116.68^0) and the dihalogen bonds C1-Cl12---Cl23 (3.56Å, 157.13^0), which are shortened by 0.375 Å with a low stabilization energy of 3.07 kcal/mol. The C19-Cl21 and C22-Cl23 bond lengths are lengthened by 0.296 and 0.060 Å, respectively. Surprisingly enough, isomer 5, stabilized by the C1-Cl12---O21 and C1-Cl12---Cl23-C22 interactions in the ground state, is altered in the excited state. The C1-Cl12---Cl23-C22 dihalogen bond is cleaved and stabilized by C2-O4…π and the halogen bond C1-Cl12---O21 as similar to isomer 8. This indicates a lower stability of the dihalogen bond. The Cl12---O21 halogen bond is lengthened by 0.49 Å, but the C2-O4…π interaction remains the same as the ground-state interaction of isomer 8. The stabilization energies of isomers 5 and 8 remain the same, 6.07 kcal/mol, indicating a similar structure in the excited state. Concerning isomers 4 and 5, isomer 4 is more stable with the ideal halogen bonds and angles.

Carbon bonded isomers (I_c)

Isomer 6, having two symmetric interactions of C-O---C (3.0.Å, 2.86Å, 87.31^0 and 94.88^0) and C-Cl---C (3.60Å, 3.57Å, 94.93^0, 93.00^0) is more stable with a favorable geometrical arrangement and a high stabilization energy of 7.01 kcal/mol. Notably, this isomer was the most stable isomer in both ground and excited state. The C7-O9---C19 and

C22-Cl23-C3 interaction is lengthened in the excited state as compared to the ground state up to 0.067Å, whereas the C19-O21---C7 and C10-Cl11---C15 interaction is shortened up to 0.098Å.

Mixed isomers (I_M)

Isomer 7, having the halogen bond C1-Cl12---O16 (3.02Å, 156.07^0), is shortened by 0.017 Å. The hydrogen bonds C18-H20---Cl12 (2.87Å, 130.11^0) and C18-H20---O4 (2.42Å, 162.16^0) are lengthened by 0.577 Å and 0.033 Å, respectively, with a low stabilization energy of 1.09 kcal/mol. The Cl2 atom is shortened in its donor and acceptor, but it is lengthened in the chain interaction. Moreover, the orientation and stability of the isomer remain the same as those of the ground state. Isomer 8, having C19-O21---π (3.05Å, 157.97^0) and C22-Cl23…O4 (3.51Å, 125.72^0) interactions, remains the same as in the ground-state orientation. The C-O---π interaction is shortened by 0.025 Å and the halogen bond is lengthened by 0.0005 Å. This is the second most stable isomer with high stabilization energy of 6.07kcal/mol. Isomer 9 has one hydrogen bond C18-H20---O4 and one C22-Cl23---C2 interaction. Surprisingly enough, C22-Cl23 ...C_2 is slightly deviated and forms a bond with the neighboring C_1 atom in the excited state. C22-Cl23---C_1 and C18-H20---O4 hydrogen bonds are shortened in the excited state by 0.04 and 0.041 Å, respectively, with stabilization energy of 4.64 kcal/mol.

An Analysis of the Ground and Excited States

While comparing the ground- and excited-state structures for all isomers, the orientation of all the excited state isomers is similar to the ground-state orientation except for isomers 5 and 9, which disturbs the relative energy stability order of excited state. The changes of the orientation are associated with the change of the bonding angle for isomer 5, which is (47.61^0) greater than the bonding-angle change in other isomers. The energy difference between the ground- and excited-state structures for all isomers is approximately 6.275 kcal/mol, except for isomer 5 (3.137 kcal/mol). Even the excited-state orientation is the same for isomers 5 and 8. Isomer 5 has the minimum energy when compared to the isomer 8 (0.001 kcal/mol). Finally, the dihalogen bond is cleaved in isomer 5 and contracted in isomer 4.

Optical Properties

The splitting of the absorption spectrum

The calculated TDDFT (M05-2X/6-31++G (d, p)) spectra for nine isomers (1–9) and monomers of DCBQ are shown in Fig. 7 and plotted as stick spectra. The superposition of the localized excitations on each monomer and the coupling between the two chromophores lead to a splitting of the monomer absorptions. This coupling will typically involve both dipole–dipole and exchange interactions. These interactions of electric dipole can be approximated by a Coulomb dipole–dipole term. Depending on the orientations and the distances between the monomers in the dimer, new oscillator strengths arise (as compared to the absorption spectra of the individual molecules), which can lead to large variations in the amplitude of spectroscopic transitions. The calculated spectra show two absorption splits for mixed isomers (I_M) 7, 8, 9 and halogen-bonded isomer (I_X) 5 only by the exciton coupling. Indeed, the splitting of isomer 5 is the largest among the four isomers. The other $I_{H,}$ $I_{X,}$ I_c isomers (1, 2, 3, 4 and 6) lack the absorption split, indicating achiral behavior. Beyond the exciton coupling, the calculated electron transition for all the isomers is the closest to the monomer transition except for isomer 6 (I_c) due to the stacking arrangement. When compared to the monomer absorption, the calculated electron transitions for all the isomers are predicted to lie at lower energy except for isomer 3 (I_H).

Transition-dipole-moment vector

The direction of the transition dipole moment is shown in Fig. 8 while its angle and distance are reported in Table 4. The value of the angles between the transition dipole moments also confirms the splitting of the absorption spectrum by exciton coupling. All the monomer and isomer transition dipoles are approximately parallel (0 or 180^0) except for isomers 7, 8, 9 (I_M) and isomer 5 (I_H), which have an acute angle. Isomer 5 (I_H), observed with the minimum angle, is found to have the largest splitting, indicating that the angle plays a vital role. The absorption broadening spectra are illustrated in the absorption spectrum with molar absorptivity Σ in Fig. S3, which predicts that the absorption width of the monomer is half the width of each isomer. It also shows the effect of the absorption-broadening band by the position and the relative orientation of the nine isomers.

The CD couplet of the CD spectrum

The monomer DCBQ is an achiral molecule and lacks optical activity. Nevertheless, chirality is deeply related to the molecular assembly on the supramolecular level. Even an achiral molecule could be possibly assembled into a chiral arrangement through non covalent interactions. Among the isomers which have different non-covalent interactions, few isomers have chiral properties indicated in the CD spectrum through exciton coupling, which is also confirmed with the optical rotation value. Through the exciton chirality method, the chirality between the two identical achiral molecules has been analyzed.

Fig. 9 shows the CD spectrum of all 9 isomers and one monomer. All of the isomers have a CD couplet between 245 and 265 nm except for the monomer and isomers 6 (I_c), 2 (I_H) and 4 (I_X). This is confirmed in the chiral nature of the DCBQ molecular arrangement. The CD spectrum reveals that isomers 7, 8, 9 (I_M), 1, 3 (I_H) and 5 (I_X) can rotate the plane of polarized light by the exciton chirality method. Isomers 1 and 3 (I_H) have a CD couplet although they are not chirally arranged. These two isomers having symmetric double hydrogen bonds are formed through the cyclic structure with oxygen and chlorine acceptors. The sign of the CD couplet is determined by the sign of its long wavelength band from Fig. 9 and reflected in the absolute sense of twist between two interacting dipoles. Among all the isomers, isomer 3 (I_H) has a long wavelength band and then isomers 7 (I_M) and 5 (I_X) have exactly the opposite CD couplet and an equal height of the peak with the same couplet crossover point, although they both have a negative-sign optical rotation value. Isomers 1 (I_H) and 9 (I_M) also have exactly the opposite CD couplet and an equal height of the peak with the same couplet crossover point like the above isomers. On the other hand, isomer 8 (I_M) only has a positive peak. The opposite peak pairs of isomers 7, 5 and 1, 9 are expressed through the interesting impact on non-covalent interactions in the exciton coupling.

The analysis of optical rotation implies that isomers 6 (I_c), 2 (I_H) and 4 (I_X) have no optical rotation value (below 0.5^0), indicating the absence of chirality, which is also proved in the CD spectrum. Isomers 7(I_M), 1(I_H) and 5 (I_X) have the negative value of optical rotation (-21.10^0, -63.32^0 and -52.67^0, respectively), indicating a negative chiral isomer. Isomers 7 (I_M) and 5 (I_X), however, have the opposite CD couplet. Isomer 5 (I_X) exhibits positive chirality in the CD spectrum and negative chirality in optical rotation. The remaining isomers 8, 9 (I_M) and 3 (I_H) are positive chiral isomers, which is reflected in the positive value of optical rotation (71.39^0, 30.48^0, 132.53^0, respectively). The CD spectra of long wavelength band are also expressed as positive chiral isomers.

The strength of exciton coupling was explained through the coupling amplitude A_{CD}, which is the intensity difference between the peak and the trough on the one hand, and the width of the couplet W_{CD} or Davydov splitting of the bands on the other. From Fig. 9, the strength of the exciton coupling for isomers through A_{CD} and W_{CD} was calculated. W_{CD} is approximately equal for all chirally arranged isomers. Isomer 3 (I_H) has a high amplitude (124.14) but without exciton coupling and isomer 9 (I_M) has a low amplitude (9.98) as compared to the other chirally arranged isomer. Isomers 7 (I_M) and 5 (I_X) have a nearly equal amplitude of 50.28 and 58.46, respectively, and for isomer 1 (I_H) the amplitude is 15.72. Overall, isomers 1, 3, 5, 7, 8 and 9 are the chirally arranged isomers. In more detail, isomers 8, 9 (I_M) and 3 (I_H) are positive chirally arranged and isomers 7 (I_M), 1(I_H) and 5 (I_X) are negative chirally arranged isomers.

The strength of exciton coupling for the isomers is in the order of 8 < 9 < 1 < 7 < 5 < 3. The exciton coupling depends on the orientation; the distance between the electric dipole moments for the corresponding monomers and the distance between the centers of mass for individual molecules are reported in Table 4. Depending on the distance between the transition dipole moments of individual molecules and the centre of mass of individual molecules, the isomers are arranged in the order of 2 < 4 < 7 < 5 = 3 < 9 < 1 < 8 < 6 and 6 < 8 < 9 < 1 < 7 < 2 < 3 < 5 < 4, respectively. Isomers 6 (I_c) and 8 (I_M) are too close based on the distance between the centers of mass. Although isomer 6 (I_P) has the less distance for center of mass between monomers, it has no chiral nature, the distance of the transition dipoles is length-associated and the isomer has no optical activity. The stability order of isomers 4, 5 (I_X) and 3 (I_H) was inversed in the order of the distance between the centers of mass.

Conclusions

The competing behavior of different non-covalent interactions (C-H…O, C-H…Cl, C-Cl…O, C-Cl…Cl-C, C-O…C, C-Cl…C and C-O…π) in the nine isomers of DCBQ dimer was analyzed and compared for ground- and excited-state properties. The following conclusions have arisen from those properties:

- The relative energy stability order for the NCIs in the nine isomers in the ground and excited states is similar: O…C > O…π > H…O > Cl…O > H…Cl > Cl...C > Cl...Cl.

- Isomer 1 (I_H) and isomer 6 (I_c) were surprisingly the most stable. The largest stabilization energy of 4.16, 5.39 and 5.67, 6.07 kcal/mol was observed for the ground and excited states at the MP2/6-31++G(d, p) level of theory, respectively.

- The orientation of all of the excited-state isomers is similar to the ground-state orientation except for isomer 5 (I_X) and isomer 9 (I_M), which disturbs the relative energy stability order. New bonds are formed in isomers 5 (I_X) and 9 (I_X) in the excited state.

- The range of increase in the donor-bond length from the ground state to the excited state is 0.0001–0.01Å.

- The transition dipoles of the DCBQ monomer and all the isomers are approximately parallel (0 or 180^0) except for isomers 7, 8, 9 (I_M) and isomer 5 (I_X), which have an acute angle.

- The CD spectrum reveals that all isomers have a CD couplet between 245 and 265 nm except for the monomer and isomer 2 (I_H), isomer 4 (I_X) and isomer 6 (I_c). This is confirmed in the chiral nature of the DCBQ molecular arrangement.

- The analysis of optical rotation indicates that isomer 2 (I_H), isomer 4 (I_X) and isomer 6 (I_c) have no optical rotation value (below 0.5^0), indicating the absence of chirality, which is also proved in the CD spectrum.

- Isomers 8 and 9 (I_M) as well as isomer 3 (I_H) are positive chirally arranged isomers and isomer 1 (I_H), isomer 5 (I_X) and isomer 7 (I_M) are negative chirally arranged isomers.

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Supplementary material:

Geometrical figures of nine isomers with noncovalent parameter computed at the M05-2X/6-31++G (d,p) level of theory were given in Fig.S1 as supplementary material. The graph for positive linear relationship between electron density and laplacian electron density for all non covalent interactions were given in Fig.S2 as supplementary material. Absorption spectrum for 9 isomers calculated at TD- M05-2X/6-31++G (d, p) level of theory were given in Fig.S3 as supplementary material. Comparison of geometrical parameters at ground and excited states were given in Table S1 as supplementary material. Monomer geometrical parameters were given in Table S2 as supplementary material. Comparisons of length shift and frequency shift were given in Table S3 as supplementary material.