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Ketocyanine Dyes: Impact of Conjugation length on Optical Absorption and Third-Order Polarizabilities

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Broken symmetry and symmetry adapted cluster-configuration interaction techniques help to understand the structure-property relationships like impact of conjugation length on the electronic structure, small energy optical absorption and third-order polarizabilities in symmetric ketocyanine dyes. The sum-over-states approximation truncated to essential states model helped to understand the origin of negative sign and the most relevant components of average static third-order polarizabilities. The results can be used as a design principle to model the ketocyanine dyes which can absorb in the visible to NIR region and show large negative third-order nonlinear activity.

1. Introduction

Linear conjugated organic molecules are the most widely studied among the various classes of functional dyes. Topologically, they belong to one of the two classes, either cyanine-like or polyene-like carbon chains. Cyanines (CY), Scheme 1, contain odd number of carbon atoms in the backbone and the π-system of these compounds is uniformly extended over the whole carbon chain and has zero bond degree. Polyenes, on the other hand, contain an even number of carbon atoms (odd number of conjugated bonds) and show a very pronounced π-electron bond alternation in the ground state.

CY dyes are relatively stable, and have high molar absorption coefficients (~10^5 M⁻¹ cm⁻¹), medium fluorescence intensity, narrow spectrum width and the ability to form H- or J-aggregates. The maximum absorption wavelength of CY can be tuned precisely from visible to near-infrared (NIR) region by chemical structural modifications. These unique photophysical and photochemical properties make CY dyes useful in many potential applications such as nonlinear optics (NLO), optical data storage, probes for biological systems, dye lasers, photorefractive materials, and photodynamic therapy.

The substitution of the hydrogen atom at the meso-position of CY by O⁻ gives rise to a ketocyanine (KCY) like chromophore, Scheme 1. This in turn perturbs the distribution of π-electrons and depending on the extent of π-conjugation; the energy gap between the Frontier molecular orbitals (FMOs) is reduced. Substitution of meso-1 and meso+1 hydrogen atoms with >C=O and -(C=O)-(O=C)- give rise to squaraine (SQ) and croconate (CR) dyes (scheme 1).

Synthesis of such KCY dyes is of current research interest due to their interesting molecular properties and serve as key components in various high-tech applications such as absorption in the long wavelength region (800-1100 nm), nonlinear optics, dye sensitized solar cells, energy transfer cascades, fluorescence bioimaging, electronic devices and so on.

Among the above mentioned applications of KCY dyes, the electronic absorption in the NIR region and NLO properties have been extensively studied due to their potential applications in electronic and optical devices. Since the chromophoric carbon chain of KCY, SQ and CR contains odd number of methine units, the spectroscopic and photophysical properties are expected to be similar to that of CY. A large number of experimental and theoretical studies have been carried out to understand the structure-property relationships in these molecules. One of the earliest calculations based on MINDO (modified neglect of differential overlap) and CNDO's (complete neglect of differential overlap/spectroscopic, single + double energy selected configuration interaction) proposed that the small energy absorption (1.98 eV) in SQ is due to the donor-acceptor-donor (D-A-D) type of chromophoric structure. Similarly, using simple Huckel Molecular Orbital (HMO) calculations and orbital symmetry considerations, Momciccholi et al. have pointed out that SQ containing even number of methine units show small HOMO-LUMO gap (HLG) while those with odd number of methine units show a large gap. In addition, our previous studies showed that these molecules are biradicaloids based on the charge transfer analysis of the excited state (excitation from S1→S2) by using the symmetry-adopted cluster-configuration interaction (SACCI) method and from the numerical biradical index (I) as well. Also, they showed a linear correlation between the biradical character and the optical absorption, and third-order polarizabilities.
2. Computational Details

All the calculations in this work have been carried out by using the Gaussian 09 ab initio/DFT quantum chemical package. The molecular geometries in the singlet ground state (S0) are energy minimized with C3v symmetry constraints using the hybrid DFT-B3LYP functional. The theoretical equilibrium S0 state geometries are obtained when the maximum internal forces acting on all the atoms and the stress are less than 4.5 × 10^{-7} eV/Å and 1.01 × 10^{-3} kBar respectively. The obtained geometries are found to be minima on the potential energy surface (PES) characterized by the real values for the vibrational frequencies at the same Hessian. The energy minimization of the triplet state (T1) geometries were also performed to check the relative stability of the S0 state. Broken symmetry (BS) approach at Hartree-Fock (HF) level is used to obtain the natural orbital occupancies of the HOMO and LUMO and to calculate the numerical values of the biradical index (Ω). These calculations were performed with Pople’s triple-ξ quality 6-311G basis set with p and d polarization functions.

3. Results and Discussion

3.1. Energy and Wavefunction Stability

The geometry optimization of the series of KCYs in their ground state with singlet closed shell (SCS) configuration were performed by increasing a single methine unit at a time symmetrically (Scheme 1, KCY structure). For easy understanding, the KCY series is separated into two sub-series i.e., odd (n_2 = 1, 3, 5 and 7) and even (n_2 = 2, 4, 6 and 8) series respectively. The odd series contains odd number of methine units on either side of CO while even series contain even number of methine units as shown in Fig. 1. It should be noted that while counting the number of methine units, the core oxayl unit should be excluded. The resonance structures for each of its kinds i.e., n_2 = 2 and n_2 = 3 are shown in Fig. 1. The

![Fig. 1 Resonance structures of odd (n_2) and even (n_2) series of KCYs.](image-url)
resonance structures $a_1$ and $b_1$ for $n_6$ series represent two valence bond structures, in which the positive charge is localized on one of the nitrogen atoms resulting charge-separated structures, whereas in $c_1$, the positive charge is delocalized over the entire carbon chain as in a typical CY. The other possibility is that either it exists in a hybrid structure $b_2$, a hybrid form of biradical and charge-separated structures, or in a neutral biradical structure $c_2$. The resonance structures $a$ and $b$ for $n_6$ series are exactly similar to that of $n_5$ series resulting in charge-separated structures, while the structure $c$ is characterized by alternating $\pi$-bonds (absence of charge-separation) and posses cross-conjugation (the set of $\pi$ bonds in aminopolyene chromophore interact with each other by conjugation excluding the other aminopolyene chromophore from interaction).

In view of the earlier predictions that in general these systems are biradicaloids (non-interacting) in nature, the wavefunction stability of the SCS configuration were therefore performed. The eigen values of stability matrix produced real values with a magnitude of 0.085, 0.056, 0.040 and 0.031 for $n_5$ series and imaginary values with almost equal magnitude of ~0.027 for $n_6$ series as shown in Table 1. The detailed meaning of these eigen values can be found in the original paper, but in general, imaginary eigen values indicate instability in the corresponding wavefunction and represents a saddle point on the PES. This signifies that in the ground state of $n_5$ series, a strong static (non-dynamical) correlation effect plays an important role. Describing such systems with single determinant methods like restricted (RH)F or RDFT yield poor description of the ground state wavefunctions and thus require an alternative method. One of the methods is the BS approach, which corrects the static correlation approximately at lower computation cost. The unrestricted (U)HF or UDFT allow for spin-symmetry breaking and approximate the static correlation correction by splitting the $\alpha$ and $\beta$ electrons into two different orbitals. Thus, the geometries of both KCY series were reoptimized at the singlet open shell (SOS) configuration using BS approach at UB3LYP. This resulted in relatively stable wavefunctions which are lower in energy than their corresponding SCS analogue for $n_5$ series. The calculated energy difference $\Delta E_1 = E_{SOS} - E_{KCY}$ is shown in Table 1 and the values increased with increasing $n_5$ (-2.58, -4.65, -5.84 and -6.65 kcal/mole for $n_5 = 2, 4, 6$ and 8) while there is no energy lowering ($\Delta E_2 = 0.0$ kcal/mole) or invoked structural changes, in comparison to the CSC configuration of $n_5$ series.

<table>
<thead>
<tr>
<th>$n_5$</th>
<th>$\Delta E_1$</th>
<th>$\Delta E_2$</th>
<th>$\Delta E_3$</th>
<th>Stability</th>
<th>($S^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.00</td>
<td>-72.34</td>
<td>0.085</td>
<td>0.00</td>
</tr>
<tr>
<td>3</td>
<td>0.00</td>
<td>0.00</td>
<td>-53.60</td>
<td>0.056</td>
<td>0.00</td>
</tr>
<tr>
<td>5</td>
<td>0.00</td>
<td>0.00</td>
<td>-43.72</td>
<td>0.040</td>
<td>0.00</td>
</tr>
<tr>
<td>7</td>
<td>0.00</td>
<td>0.00</td>
<td>-37.67</td>
<td>0.031</td>
<td>0.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$n_6$</th>
<th>$\Delta E_1$</th>
<th>$\Delta E_2$</th>
<th>$\Delta E_3$</th>
<th>Stability</th>
<th>($S^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-2.58</td>
<td>-4.98</td>
<td>-7.99</td>
<td>-0.022</td>
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</tr>
<tr>
<td>4</td>
<td>-4.65</td>
<td>-6.43</td>
<td>-4.60</td>
<td>-0.027</td>
<td>0.81</td>
</tr>
<tr>
<td>6</td>
<td>-5.84</td>
<td>-7.21</td>
<td>-3.11</td>
<td>-0.029</td>
<td>0.92</td>
</tr>
<tr>
<td>8</td>
<td>-6.65</td>
<td>-7.72</td>
<td>-2.28</td>
<td>-0.029</td>
<td>1.00</td>
</tr>
</tbody>
</table>

It is also worth noting that the singlet biradical form of $n_6$ series is largely contaminated by higher spin states ($S^2$) values are different from 0 (pure singlet) or 2 (pure triplet) as shown in Table 1.

The spin contamination of the biradical state grows from 0.61–1.00 and this may be the likely result of the energy gap between the $S_0$ and $T_1$ states becoming smaller as the size of $n_6$ increases. Although ($S^2$) is not rigorously defined in DFT, spin contamination makes additional stability of the singlet open shell configuration (biradical form) relative to the singlet closed shell configuration. However, a heavily spin contaminated wavefunction in principle will affect properties such as total energy, optimized geometry and excited state energies and so on, as it originates in the unrestricted wavefunction itself. In order to eliminate this error, the approximate spin projection (AP) technique has been used where the total energy is given by eq.(4):

$$\frac{i}{2} E_o(t) -\frac{i}{2} E_o(\bar{t}) = \frac{i}{2} E_o(t) -\frac{i}{2} E_o(\bar{t}) = \frac{i}{2} \langle \xi | \frac{\partial H}{\partial t} | \xi \rangle_{\bar{t}}$$

The quantities $E$ and $\overline{E}$ in the above equation are the total energies of low and high spin states. The energy of the SOS wavefunction within this approximation for $n_5$ series is further lowered energetically by 1.07–2.40 kcal/mole ($\Delta E_2$) and hence increase in the $S_0-T_1$ energy gap ($\Delta E_1$). No energy lowering or increase of $\Delta E_2$ is observed for $n_6$ series. However, in both the series, the energy gap is decreased with increase in number of methine units. Beyond $n_5$, the SOS configuration becomes unstable and $T_1$ becomes relatively more stable than $S_0$. Similarly, the stability of $T_1$ for $n_5$ can be seen after 17-methine units in the aminopolynylene chain (linear fit).

3.2. Soliton Structure and Bond Length Alternation:

As shown in Scheme 1, the KCY and its derivatives have same number of methine units in the carbon backbone as in CY. CYS possesses a distinguishing feature of alternating charges (charge wave or soliton), thus a similar charge wave is expected in KCYs. Alternately, the soliton can be described as a function of charge alternation at the neighbouring $\pi$-centres; $\Delta q = |q_i - q_{i+1}|$, where $q$ is the charge at the $\pi$-center. Fig. 2 shows plots of $q_i$ and $\Delta q_i$ based on the Mulliken atomic charges and reveals the following facts. (i) The presence of oxygen atom at the meso-position of the carbon backbone in KCY’s reduced charge at the meso-carbon atom by 0.55 e. (ii) Both the odd and even series showed charge alternation. Except at $C_2$, $C_3$ and $C_4$, $C_5$ positions in even series, charge alternation is not observed (shaded region in Fig. 2). (iii) The attenuation of the soliton from the centre is very slow compared to CY with same carbon chain length.
The local bond length alternation of the neighbouring C–C bonds described by \( \Delta l = |l_i - l_{i+1}| \), where \( l \) is the length of the \( i^{th} \) C–C bond in the backbone.\(^{71} \) The corresponding \( \Delta l \) values for each of the cyanine series is shown in Fig. 3. The \( \Delta l \) in the case of \( n_o \) series for \((C_2−C_3)−(C_3−C_4)\) is almost constant with a value in between 0.122–0.125 Å and for the remaining \( \Delta l \) along the carbon chain for each \( n_o \), a constant value of ~0.078 Å is obtained. This is in line with the resonance structure \( c \) in Fig. 1. Further increase in \( n_o \) would not give a significant rise in BLA suggesting the saturation limit.

Contrary to the \( n_o \) series, the \( n_e \) series showed a different behaviour as evident from the \( \Delta l \) values. The \((C_2−C_3)−(C_3−C_4)\) bond distance is continuously increased with \( n_e \) by 0.056–0.101 Å, while the rest of the \( \Delta l \) in each \( n_e \) is continuously increased except at \((C_4−C_5)−(C_5−C_6)\) in \( n_e = 6 \) and \((C_5−C_6)−(C_6−C_7)\) in \( n_e = 8 \), the increase is very small (BLA of ~0.003 Å).

Fig. 2 Charge alternations in the \( n_o \) and \( n_e \) series of KCYs.

Fig. 3 Local BLA in the \( n_o \) and \( n_e \) series of KCYs.
3.3. Singlet Biradical Character:

According to the values of $\Delta E_1$ and $\Delta E_2$ in Table 1, KCYs corresponding to the $n_e$ series are biradicals, the less favorable singlet states which are best described by the SB method and qualitatively show pronounced biradical character. A singlet biradical can be defined as a molecular species that has all electrons paired, but a pair of these electrons occupies different parts of space with a small shared region. Fig. 4. The ground state of such species is a singlet, yet they exhibit biradical character. On the other hand, a pure biradical is a molecular species with two electrons occupying two degenerate, or nearly degenerate, molecular orbitals.

Quantitatively, the numerical values of the biradical character in the singlet ground state are estimated using the SB approach at UHF level and the obtained values are presented in Table 2.\(^3\) The biradical index $Y_f$ related to the HOMO and LUMO for singlet states, is defined by the weight of the doubly-excited configuration in the multi-configuration (MC)-SCF theory, and is formally expressed in the case of the spin-projected UHF (PUHF) theory as\(^3\)

$$Y_f = 1 - \frac{2T_f}{1 + T_f^2}$$

where $T_f$ is the orbital overlap between the corresponding orbital pairs, and can be calculated using the occupation numbers of UHF natural orbitals.

$$T_f = \frac{\eta_{\text{HOMO}} - \eta_{\text{LUMO}}}{2}$$

It is worth pointing out that the biradical index ranges from 0 % for the SCS configuration to 100 % for the pure biradical state. As $n_e$ series is stable in SCS configuration, it has $Y_f$ of 0 %. The $Y_f$ value for $n_e$ series is found in the range between ~53–86 %. In addition, $Y_f$ increases with decrease in orbital overlap $T_f$. It turns out that, in spite of the simplicity of the scheme using the unrestricted natural orbitals (UNOs), it successfully reproduced the biradical character of the investigated molecules. Also, it is seen that $Y_f$ is linearly dependent on the $C_3$-$C_2$-$C_1$ bond angle, which is in line with our earlier predictions.\(^4\) For $n_e$ series, a constant value of 115.9° is obtained while for $n_e$ series, it increased by a very small value of -0.37° and range between 112.2–113.3°, suggesting that a very small increase in angle is sufficient to produce large $Y_f$ in the $S_0$ state.

### Table 2

<table>
<thead>
<tr>
<th>$n_e$</th>
<th>$\angle C_3$-$C_2$-$C_1$</th>
<th>$\eta_{\text{HOMO}}$</th>
<th>$\eta_{\text{LUMO}}$</th>
<th>$T_f$</th>
<th>$Y_f$%</th>
<th>HLG</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>115.9</td>
<td>2.000</td>
<td>0.000</td>
<td>1.000</td>
<td>4.77</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>115.9</td>
<td>1.827</td>
<td>0.173</td>
<td>0.827</td>
<td>3.66</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>115.9</td>
<td>1.652</td>
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<td>0.652</td>
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</tr>
<tr>
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<td>15</td>
</tr>
<tr>
<td>2</td>
<td>112.2</td>
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<td>0.750</td>
<td>0.250</td>
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<td>0.854</td>
<td>0.146</td>
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</tr>
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<td>6</td>
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<td>0.098</td>
<td>81</td>
<td>0.92</td>
</tr>
<tr>
<td>8</td>
<td>113.3</td>
<td>1.072</td>
<td>0.928</td>
<td>0.071</td>
<td>86</td>
<td>0.76</td>
</tr>
</tbody>
</table>

The spatial biradical distribution is examined in the singlet biradical structures by inspecting the HOMOs and LUMOs for the $\alpha$ and $\beta$ spin electrons. The frontier orbitals for the $\alpha$ and $\beta$ spin electrons of $n_e = 5$ and $n_e = 6$, calculated using the SB method are depicted in Fig. 4. The $\alpha$-HOMO and $\beta$-HOMO, as well as the $\alpha$-LUMO and $\beta$-LUMO, are of almost identical shapes for $n_e = 5$ (Fig. 4, top). The HOMO and LUMO are occupied with 1.652 and 0.348 electrons, respectively. In addition, there is a noticeable shared region between the HOMO and LUMO, which is in agreement with the large $T_f$ value of 0.652 (Table 2). The situation is quite different in $n_e = 6$ (Fig. 4, bottom). A remarkable feature is that the $\alpha$-HOMO and $\beta$-LUMO occupy practically the same part of the space, involving approximately 1.098 and 0.902 electrons. The same situation is found in the case of the $\beta$-HOMO and $\alpha$-LUMO. In this way, there are no unpaired electrons in even system, yet two of them occupy different parts of the space with a small shared region indicating that the ground state is singlet biradical and thus allowing the $\pi$-electrons to delocalize.

![Fig. 4](Image) Frontier one electron molecular orbitals of the KCYs for $n_e = 5$ (top) and $n_e = 6$ (bottom).

It is also important to inspect the spin densities of the singlet biradicals. The Mulliken spin density distribution at each carbon atom of the chain for $n_e$ series is shown in Figure of Table 3 while the sum of spin densities on the left and right side of the $meso$-position and the spin densities at the $C_3$ and $C_7$ carbon atoms are presented in Table 3. The very small or negligible spin density alternation (spin up $(\uparrow)$ and spin down $(\downarrow)$) along the $\pi$-conjugation in $n_e$ series does not confirm the spin alternation and indeed indicate the absence of the biradical character. The sums of spin densities in $n_e$ series increase with conjugation length due to the delocalization of spins over the $\pi$-conjugation and decrease at $C_3$ and $C_7$ atoms. This indeed implies that the coupling between the unpaired electrons is reduced leading to large biradical character. For shorter chain lengths, the spins localize at $C_3$, $C_7$ positions and start moving towards the centre of the aminopolyenic chromophores with increasing length. Moreover, the spin densities with opposite signs on either side of the $meso$-position indicate the localization of the spin up $(\uparrow)$ and spin down $(\downarrow)$ electrons and hence the stability of the singlet biradical in the ground state. Beyond the critical value for $n_e$, a simple inversion in the sign of spin density from negative to positive or vice-versa occurs which leads to the stability of the triplet state. Since the biradical character for $n_e = 2$ is ~50%, it is not possible to predict the spin densities.
LUMO with increasing coefficient at C
coefficients at C
smaller than C
retains the KCY character. Interestingly, the coefficients at C
characterized by a large contribution consequently the energy of the HOMO is raised. The LUMO is coefficients at C
positions C
the HOMO level. The coefficients at C
state. One would expect a little contribution from these two atoms to (concentration of electron density at C
atoms, which primarily indicates that it lacks the KCY character and stabilization of LUMO level from
chain length dependence of
levels for both the series is shown in Fig.
A comparison of five highest occupied and five lowest unoccupied (Fig.
coefficients for the HOMO and LUMO.
Contrary to
series, the HOMO in each of the
series is characterized by a large coefficient at O1 and C2 atoms indicating that the KCY character is maintained. Increasing
the coefficient at O1 is decreased (0.64–0.43) while a constant coefficient at C2 (0.11) is maintained Fig. 6 (bottom). As seen in Fig. 5, the constant position of HOMO level at -3.8 eV with
is attributed to the constant coefficient at C2 atom. The coefficients at the rest of the carbon atoms along the chain have similar coefficients as in
series. The LUMO in this series is characterized by a nodal plane through O1 and C2 atoms and the coefficients at C3, C6, C7, and C9 (equivalent positions C3, C5, C7, and C9) are relatively larger than those in the HOMO while the coefficients at C4, C6, C8 and C10 (C4, C6, C8, C10) is negligible. The continuous stabilization of LUMO (from -2.22 to -3.0 eV) is attributed to the decrease in the coefficients at C3 and C5. Thus the decrease of HLG in
series is LUMO driven.

### 3.4. Frontier Molecular Orbitals

A comparison of five highest occupied and five lowest unoccupied levels for both the series is shown in Fig. 5. The sensitivity of the chain length dependence of
series can be seen from the continuous destabilization of the HOMO level from -5.6 to -4.8 eV and stabilization of LUMO level from -0.78 to -2.11 eV. This can be explained based on the atomic coefficients for the HOMO and LUMO orbitals as depicted in Fig. 6 (top). The HOMO in each of the
series is characterized by a nodal plane through O1 and C2 atoms, which primarily indicates that it lacks the KCY character (concentration of electron density at C5-C7-C9 atoms) in the S0 state. One would expect a little contribution from these two atoms to the HOMO level. The coefficients at C3, C5, C7, and C9 (equivalent positions C3, C5, C7, and C9) are relatively larger than those at C4, C6, C8 and C10 (C4, C6, C8, C10) atoms. Also, the coefficients decrease along the polymethine chain as
increases. Moreover, the coefficients at C3 and C5 continuously decrease (0.57–0.34) and consequently the energy of the HOMO is raised. The LUMO is characterized by a large contribution from O1 and C2 atoms such that increasing the
is expected to affect the LUMO and the
series retains the KCY character. Interestingly, the coefficients at C3, C5, C7, and C9 (equivalent positions C3, C5, C7, and C9) are relatively smaller than those at C4, C6, C8 and C10 (C4, C6, C8, C10). The coefficients at C3 and C5 are in phase with C2 and therefore the increase of coefficient at C3 and C5 continuously stabilize the LUMO with increasing
. At the same time the coefficient at C3 and \(C_Y\) in the HOMO are in out of phase relation with the C2 therefore decrease of the coefficient at C3 and C5 continuously destabilize the HOMO with increasing
. This consequently decreases the HLG with increasing
(Fig. 5). This suggests that the decrease of HLG is driven by both HOMO and LUMO.

\[
\begin{array}{cccc|c|c|c|c|c|c}
\text{Table 3} & \text{Singlet ground state spin densities of } n_e \text{ series located at each carbon atom of the polymethine (figure) and at C3 and C}\_Y & \text{carbon atoms and summed spin densities located at left and right polymethine chains.} \\
\hline
n_e & \text{Spin densities} & \text{C}\_1 & \text{C}\_Y & \text{Left chain} & \text{C}\_1 & \text{C}\_Y & \text{Right chain} \\
\hline
4 & \begin{array}{cccc}
0.120 & 0.158 & 0.000 & -0.158 & 0.120 \\
-0.273 & -0.360 & -0.382 & 0.360 & 0.273 \\
\end{array} \\
6 & \begin{array}{cccc}
0.108 & 0.167 & 0.090 & -0.167 & -0.108 \\
-0.231 & -0.324 & -0.247 & 0.234 & 0.231 \\
\end{array} \\
8 & \begin{array}{cccc}
0.100 & 0.158 & 0.176 & 0.000 & -0.148 & -0.176 & -0.158 & -0.100 \\
-0.199 & -0.298 & -0.326 & -0.295 & 0.295 & 0.326 & 0.299 & 0.199 \\
\end{array} \\
\hline
\end{array}
\]

Fig. 5 Evolution of energy levels of five highest occupied and five lowest unoccupied levels of \(n_o\) and \(n_e\) series of KCYs.
3.5. Vertical Electronic Transition Energies

The photophysical properties of both the series of KCYs are qualitatively well described by the “free electron” model and represented by two potential boxes corresponding to the two aminopolyenic chromophore units separated by a potential barrier while the length of the chromophore corresponds to the width of the box, Fig. 7. The barrier is due to the presence of C=O group. The difference between both the series lies in the strength of coupling between aminopolyene chromophores with CO group. The barrier is so high in the $n_o$ series due to the very small coupling between the two aminopolyenic chromophores (cross-conjugation) and it vanishes in the even series due to the strong coupling of the chromophores (increased conjugation). Depending upon the strength of the coupling between the aminopolyenic chromophores, the electronic coupling between the excited singlet states in both the series can occur in two ways as shown in the Fig. 7. (i) dipole-dipole interaction and (ii) conjugation through the potential barrier and corresponds to the electron tunnelling through the barrier. The dipole-dipole interaction in odd systems is very weak due to the presence of cross-conjugation (aminopolyeneal and aminopolyene are treated as isolated dipoles). This interaction gives the small symmetric splitting ($\Delta\nu$, a measure of the chromophore interaction) between the $S_1$ and $S_2$ states that is so that the final splitting becomes unsymmetric (Fig. 7). This will relatively decrease $E_{01}$ and increase $E_{02}$ by making $S_0 \rightarrow S_2$ transition symmetrically forbidden for both one- and two-photon absorption.

### HOMO and LUMO Coefficients for Odd (top) and Even (bottom) KCY series

<table>
<thead>
<tr>
<th>$n_o$</th>
<th>HOMO</th>
<th>LUMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1" alt="HOMO Coefficients for $n_o = 1$" /></td>
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<td>$n_e$</td>
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<td>LUMO</td>
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</table>
deviation is due to the fact that the measurements were performed in the solution phase while the calculations are performed in the gas phase. Though quantitatively the experimental values cannot be reproduced, the trends and the responsible factors can be reasoned. At the orbital level these transitions are described as a single particle-hole excitation from the HOMO→LUMO (α→β) level with a single |c| of 0.944, 0.935, 0.914 and 0.893 respectively as depicted in Fig. 4. These transitions are also accompanied by a less prominent but with significant |c| value of 0.125, 0.200, 0.268 and 0.323 along the series from low lying occupied to higher lying unoccupied orbitals HOMO-1→LUMO+3/HOMO-1→LUMO+1 (b→a/b→α). These large energy transitions in n₀ series are in fact due to the presence of cross-conjugation (no interaction between amionopolyene and amonopolyene chromophores, structure c of Fig. 1) which reduces the effective conjugation length. The decrease in the $E_{01}$ energy with increase in n₀ is due to the delocalization of the π-electron cloud across amionopolyene chromophore. At the same time, increasing the conjugation on the other amonopolyene chromophore has no impact on these transitions but simply extends the conjugation length. The very small increase from n₀ = 5 to 7 suggests the saturation limit which is evident from the large BLA value of 0.08 Å (Fig. 3). Beyond this optimal length of n₀ = 7, the BLA would reach the maximum value of 0.1 Å, equivalent to that of typical polylene and thus would not show further decrease in $E_{01}$. The second lowest transition energies $E_{02}$ (S₀→S₂/π→π⁻, two-photon state) appeared at 5.04, 4.41, 3.96 and 3.95 eV ($1'4'→3'4'$) are produced with a large intensity as evident from their respective μ₀ values of 7.1, 10.1, 12.9 and 15.5 D and are polarized along π-direction. These values are in good agreement with the energy gap (HLG) of 4.77, 3.66, 3.06 and 2.68 eV as shown in Table 2. The calculated trend is in good agreement with the experiment but the values differ by ~1.32 eV (experimentally determined values are 3.54, 2.64 and 2.25 eV for n₀ = 1, 3 and 5 respectively). This Table 4 Calculated S₀→S₁ and S₀→S₂ transition energies ($E_{0n}$, eV), S₀ and S₁ permanent dipole moments and S₀→S₁ transition dipole moments (μ₀, μ₁ and μ₀1, D), nature of the transitions ($C_{i}^{\text{singlets}} \geq 0.1$ & $C_{doubles} \geq 0.2$) and splitting between S₁ and S₂ states ($\Delta \nu$, cm⁻¹). The directions of the dipole moments are given in parenthesis. For n = 2 for S₀→S₁ and S₀→S₂ respectively for both the series of KCYs.

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<th>Nature of Transition</th>
<th>$\Delta \nu$</th>
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<td>1.1(z)</td>
<td>0.917 (H-1→L)</td>
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<td>4.0(z)</td>
<td>10.1(y)</td>
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<td>0.4(z)</td>
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<td>12.9(y)</td>
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<td>3.96</td>
<td>$1'4'→3'4'$</td>
<td>3.3(z)</td>
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<td>$1'4'→3'4'$</td>
<td>2.9(z)</td>
<td>0.6(z)</td>
<td>0.902 (H-1→L)-0.222 (H→L+1)</td>
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<table>
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<tr>
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<td>1.9(z)</td>
<td>0.6(z)</td>
<td>0.603 (H→L+1)+0.361 (H-3→L)-0.503 (H→L+1; H→L)</td>
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<td>1.3(z)</td>
<td>-0.559 (H→L-1)-0.394 (H-2→L)-0.517 (H→L+1; H→L)</td>
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<td>3.6(z)</td>
<td>19.1(y)</td>
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<td>3.7(z)</td>
<td>0.5(z)</td>
<td>-0.381 (H→L+1)+0.282 (H-5→L)-0.641 (H→L; H→L)</td>
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<td>$1'4'→1'B$</td>
<td>4.3(z)</td>
<td>3.9(z)</td>
<td>22.8(y)</td>
<td>0.902 (H→L)+0.143 (H-4→L)-0.272 (H-1→L+1)</td>
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<td>4.43</td>
<td>$1'4'→2'4'$</td>
<td>3.0(z)</td>
<td>0.4(z)</td>
<td>-0.445 (H→L-1)-0.249 (H-5→L)+0.619 (H→L; H→L)</td>
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The $E_{\text{01}}$ energies of $n_\pi$ series are relatively small compared to $n_\sigma$ series and showed absorption in the NIR region. The $E_{\text{01}}$ (S1$\rightarrow$S0/\pi$\rightarrow$\pi$^*\rightarrow$) values are 1.57 ($n_\sigma = 2$), 1.21 ($n_\sigma = 4$), 1.21 ($n_\sigma = 6$) and 1.25 ($n_\sigma = 8$) eV (1.4' $\rightarrow$ 1.4') respectively. These values are also in good agreement with HLG (Table 2). These transitions are appeared with large intensity as evident from their respective $\mu_{\text{01}}$ values of 9.7, 14.4, 19.1 and 22.8 D. These transitions are similar to $n_\sigma$ series but differ in the supplememt transition. These are described as HOMO-2$\rightarrow$LUMO/HOMO-4$\rightarrow$LUMO (b$\rightarrow$a/b$\rightarrow$a) for the intermediate and large biradical systems. In addition to the singles CI, these are accompanied with doubles CI (common for biradicals) from HOMO$\rightarrow$LUMO-1; HOMO$\rightarrow$LUMO-3 (b$\rightarrow$h; b$\rightarrow$e) with $|c_2|=0.234, 0.240, 0.243$ and 0.272 respectively. As discussed earlier, the $n_\sigma$ series lose the oxalyx characteristic (biradical nature and the concentration of electron density at the center) and increase in $E_{\text{01}}$ values at $n_\sigma$ = 7. This is evident from the continuous increase in BLA up to 0.06 Å (Fig. 3) and has been proved experimentally and theoretically for extended squaraines. 

The second lowest transitions are $z$-polarized and the energies are 3.05, 2.45, 4.23 and 4.43 eV (1.4'$\rightarrow$2.4'$\rightarrow$1.4'$\rightarrow$4.4') (A). These have relatively small intensity as seen from the $\mu_{\text{02}}$ values (Table 3). These transitions are different from $n_\sigma$ series and described as HOMO$\rightarrow$LUMO+1 (b$\rightarrow$h) and accompanied by single and doubles excitations HOMO$\rightarrow$LUMO/HOMO-3$\rightarrow$LUMO/HOMO-5$\rightarrow$LUMO (b$\rightarrow$h). The very large splitting, 2.45 Å between the $S_1$ and $S_2$ states of 119, 19760, 24360 and 25650 cm$^{-1}$ (1.49, 4.25, 3.02 and 3.18 eV) for $n_\sigma$ = 2, 4, 6 and 8 suggest that the interaction between the aminopoleynal and aminopoleynalchromophores is very strong and increase with $n_\sigma$. This makes the two-photon transition between the $S_0$ and $S_2$ states symmetrically forbidden.

The constant $\mu_0$ values of 4.5 D for $n_\sigma$ indicate the presence of neutral biradical form in the $S_0$ state while the increase of $\mu_1$ (both $n_\sigma$ and $n_\sigma$ series) in the $S_1$ state represent the charge-separated form. At sufficiently long chain length, both these systems might undergo symmetry-breaking in the excited state. This is in contrast to the typical CY which show nearly equivalent $\mu_0$ and $\mu_1$ values up to a critical value of $n$, but under goes symmetry-breaking in the ground state at sufficiently long chain lengths.

Based on these structure-property relations, it can be explained that the small energy absorption of 1.13 eV for BM1 dye reported by Langhals et al.$^{77}$ is due to the fact that it belongs to even series of KCYs and thus have a large biradical character. Extension by methine group on either side produces BM2 (furan to pyran),$^{78}$ which showed absorption energy of 2.76 eV and thus belongs to odd KCY series and thus possess small biradical character. Similarly, these relationships can applicable to explain the absorption of SQ and CR dyes reported by several authors.$^{8,23,29,44,79}$

**Fig. 8** Example of KCY dyes with even and odd methane units.

### 3.6. Third-Order Polarizabilities:

The average static (at zero frequency) third-order polarizabilities, $\gamma$ were calculated by fitting the quantities obtained from SACC calculations into eq.(1) to eq.(3). The eq.(1) and eq.(2) assist to elucidate the major structural aspects that influence the origin of negative sign and the large magnitudes of KCYs. The T-term is calculated by considering the second excited state (two-photon state) that is strongly coupled to the first excited state with large transition dipole moments, $\mu_2$. The calculated values for each of the D, N and T-terms ($\gamma_D$, $\gamma_N$ and $\gamma_T$) and $\gamma$ are presented in Table 5. Irrespective of odd or even series, symmetric KCYs are characterized by non-vanishing dipole moments in $S_0$, $S_1$ and $S_2$ states along $z$-direction ($C_z$ symmetry) while the difference in dipole moment ($\Delta\mu_{z,z}$) remains only in the $z$-component. The molecular long axis is taken as $y$ and $x$ is perpendicular to the approximate plane of the molecule therefore the transition dipole moment between the two states, $S_0$$\rightarrow$$S_1$ ($\mu_{01}$) or $S_1$$\rightarrow$$S_2$ ($\mu_{12}$) is limited to $x$ and $y$-directions. By using these symmetry relations, eq.(1) and eq.(2) are reduced to eq.(5) and eq.(6) as shown:

$$\gamma_D = 24 \left\{ \left[ \frac{\langle \mu^{\alpha}_{\gamma} \rangle}{\langle E_{01} \rangle} \right] \left[ \frac{\langle \mu^{\alpha}_{\gamma} \rangle}{\langle E_{02} \rangle} \right] \right\} - \gamma_0 + \gamma'_{01}; \quad \gamma^L_{01} = \gamma_{01} - \gamma'_{01}$$

$$\gamma_N = 4 \left\{ \frac{\langle \mu^b_{\gamma,\gamma} \rangle}{\langle E_{01} \rangle} \right\} - \gamma^L_{01}; \quad \gamma^L_{01} = \gamma_{01} - \gamma'_{01}$$

$$\gamma_T = 4 \left\{ \frac{\langle \mu^b_{\gamma,\gamma} \rangle}{\langle E_{01} \rangle} \right\} + 4 \left\{ \langle \mu^b_{\gamma,\gamma} \rangle \langle \mu^b_{\gamma,\gamma} \rangle \langle \mu^b_{\gamma,\gamma} \rangle \langle \mu^b_{\gamma,\gamma} \rangle \right\} \right\} - \gamma^L_{01}; \quad \gamma^L_{01} = \gamma_{01} - \gamma'_{01}$$

Under the three-state approximation, the $z$-component $\gamma_{zz}$ is vanished. From the table it is seen that both the series possess negative $\gamma$ values mainly originate from the $S_0$$\rightarrow$$S_1$ transition dipole moments (7.1−15.5 D, 9.7−22.8 D for both the series) indicating the predominance of $\gamma_T$ term. Moreover, the values of $n_\sigma$ series is 2−4 orders of magnitude larger than the $n_\sigma$ series. The factors to these contributions can be depicted in detail as follows. (i) The small $S_0$ and $S_1$ state dipole moment difference ($\Delta\mu_{01}$) (0.4−2.1 D) which produce non-compensating and insignificant contribution of $< 2.0 \%$ (0.3−3.3×10$^{-5}$ esu and 39.6−14.9×10$^{-6}$ esu) from the D-term ($\gamma_D$ and $\gamma_N$) in both the series. These small values are originated by the amino groups, which are projected in x-direction (as the hydrogen atoms of amino group is projected in x-direction). (ii) A very large significant reduction of the $\gamma$ values in $n_\sigma$ series by 43−98 % is mainly due to compensatory contributions from the $\gamma_T$ term (10.4−1702.5×10$^{-36}$ esu) originating from $S_0$$\rightarrow$$S_1$ ($1^1B$$\rightarrow$$2^1A$) transition dipole moments, $\mu_{12}$ of 4.7−16.6 D (two-photon transition probability). Moreover, $S_0$ and $S_1$ transition, which is one-photon forbidden in centro-symmetric systems, becomes two-photon allowed with $y$ polarization due to small $S_0$$\rightarrow$$S_1$ energy gap (0.09−0.58 eV) (Table 4). (iii) In the case of even series, the large values originate from very large $S_0$$\rightarrow$$S_1$ transition dipole moments (9.7−22.8 D) and introduces ~12.0 % (252.8−2811.9×10$^{-36}$ esu) compensating contribution originating from the small $\mu_{12}$ (4.0−5.5 D) due to large $S_1$$\rightarrow$$S_2$ energy gap (1.24−3.18 eV), making $\gamma_D$ to be very large negative (as in ideal CYs). Thus, very large $\mu_{12}$ transition dipole moment represents a crucial factor that discriminates the $n_\sigma$ and $n_\sigma$ series of KCYs. However, for both $\gamma_D$ and $\gamma_T$, the $\gamma$-component ($\gamma_{zz}$) dominates over $x (< 1.5 \%)$ due to the large transition moments in $y$-direction (along the carbon chain). In contrast, the symmetric CYs have a strong contribution from $S_0$$\rightarrow$$S_1$ transition giving rise to large negative $\gamma$ while for the asymmetric CYs (beyond the critical chain length where the onset of symmetry-breaking occurs), $\gamma$ is large and positive due to the compensating contribution from the D- and T-terms. The contribution from the higher excited states is negligible, as the transitions from ground to higher excited states ($S_1$$\rightarrow$$S_2$; $i \geq 2$) and from first excited state to the higher two-photon states ($S_i$$\rightarrow$$S_j$; $j > 3$) are associated with large $E_{02}$.
4. Conclusions

We have performed detailed calculations to understand the electronic structure, optical absorption and third-order polarizabilities of symmetric KCYs containing odd and even number of methine units in the carbon backbone. The results address the following predictions. (i) The very small interaction between the aminopolyeneal and aminopolyene chromophores in odd series of symmetric KCYs containing odd and even number of symmetric KCYs suggests that these are cross-conjugated systems and the instability of the closed shell ground state wavefunction of even series suggests that they exist in the form of biradicals. (ii) The presence of cross-conjugation reduces the effective conjugation length which is reflected in the large $S_0 \rightarrow S_1$ transition energies (blue region of the spectrum). The biradicaloid character or the mixture of biradical and charge-separated forms increases the overlap between the two chromophores and consequently reduces the HLG. This is clearly reflected in the small and intense $S_0 \rightarrow S_1$ transition energies (NIR region). (iii) Overall this leads to a large negative values for $\langle \gamma \rangle$. The relatively small $\langle \gamma \rangle$ values in the odd series is predicted to be the compensating contribution from the T-term and originated from the large $S_1 \rightarrow S_2$ transition dipole moments due to small energy splitting between $S_1$ and $S_2$ states. The large negative values in the even series is originated from the large $S_0 \rightarrow S_1$ transition moments and very small compensating contribution from the $S_1 \rightarrow S_2$ transition moments due to the large splitting between the $S_1$ and $S_2$ states. (iv) The results also suggests that odd series requires at least three-states, while even series requires two-states to model the KCYs and to determine the values of $\langle \gamma \rangle$. Thus, in short, excluding the core oxaylal part, KCYs containing odd number of methine units absorbs in visible region and show small negative $\langle \gamma \rangle$ while KCYs with even number of methine units absorb in the NIR region and show large negative $\langle \gamma \rangle$. Depending up on the type of application, this can be used as design principles for KCY systems for tuning the optical absorption from the visible to NIR region and subsequently leading to large third-order polarizabilities.

Acknowledgement

EDJ and KY thank Department of Science and Technology (DST), New Delhi for the support under J. C. Bose Fellowship. We also thank Center for Molecular Simulation and Design (CMSD), University of Hyderabad for computational facilities.

Notes and references


Table 5 Calculated $S_0 \rightarrow S_1$ and $S_1 \rightarrow S_2$ transition dipole moments, contributions of dipolar, negative and two-photon terms $(\gamma^D, \gamma^{\text{neg}}$ and $\gamma^T, \times 10^{-36}$ esu) and average $\langle \gamma \rangle$ at 2-state and 3-state model $(\langle \gamma \rangle^{\text{2-state}}$ and $\langle \gamma \rangle^{\text{3-state}}, \times 10^{-36}$ esu) for both the series of KCYs.

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<th>$\mu_0$</th>
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<th>$\gamma^{\text{neg}}$</th>
<th>$\gamma^T$</th>
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