

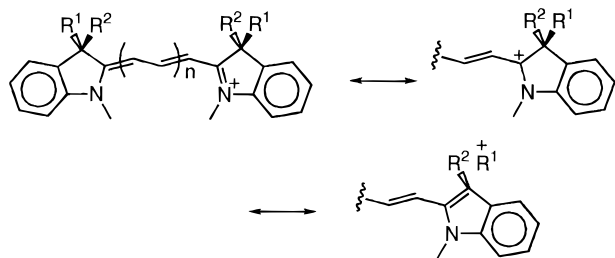
Hyperconjugation Discriminates between Helically Twisted Cyanine Dyes

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Cyanine dyes represent a remarkable class of organic dyes, with applications ranging from spectral sensitization to nonlinear optics and optical data storage.¹ The unique electronic structure that makes these applications possible is caused by a topological peculiarity: the delocalization of an even number of π -electrons over an uneven number of π -centers.² As a consequence, π -density alternation, which leads to double bond fixation in open-chain conjugated polyenes, is shifted to the atomic centers along the chromophore instead. Spectral evidence, e.g.,



the analysis of ¹³C NMR chemical shifts,³ is in accord with a description that localizes positive charge on every other carbon atom of the chromophore. Formally, these charges can also be shifted, via non-bonding resonance forms, into saturated positions of the molecule. We present experimental and theoretical evidence to show that this kind of interaction does indeed take place. In particular, hyperconjugation is responsible for chiral discrimination observed in helically twisted indocyanine dyes.

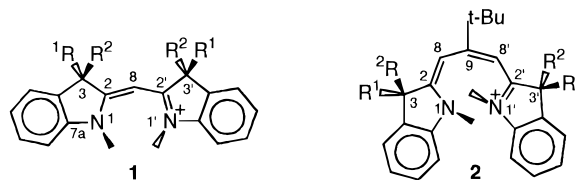
In the all-(*Z*)-configured cyanine dyes **1** and **2**, steric interactions induce a helical twist into the chromophore, with the end groups being mutually rotated by 45° (**1a**)⁴ and 41° (**2a**),⁵ according to X-ray structure analyses. In solution, a dynamic equilibrium between the two oppositely twisted enantiomeric conformations is established.³ Substituting one of the geminal methyl groups by a propyl group, as in **1b** and **2b**, renders the conformations chemically different, i.e., chiral discrimination

Table 1. Experimental^a and Calculated Bond Lengths (in pm) and Dihedral Angles (in deg) of Helically Twisted Cyanine Dyes

| | C3–R ¹ | R ¹ –C3–C2–N1 | C3–R ² | R ² –C3–C2–N1 |
|-----------|---------------------|--------------------------|-------------------|--------------------------|
| 1a | <i>152.3; 153.7</i> | <i>123</i> | <i>152.7</i> | <i>–116</i> |
| | 153.8 | 125 | 154.3 | –112 |
| 2a | <i>151.1</i> | <i>–132</i> | <i>154.6</i> | <i>104</i> |
| | 153.5 | –131 | 154.8 | 106 |

^a In italics; **1a** from ref 4, **2a** from ref 5. Data for the two crystallographically different sites at C3 and C3' have been averaged according to C2 symmetry except for the first entry of the first row, where the data differ strongly.

is established.⁶ The mechanism by which alkyl substitu-



| | R ¹ | R ² |
|---------------|-----------------|---|
| 1a, 2a | CH ₃ | CH ₃ |
| 1b, 2b | CH ₃ | CH ₂ CH ₂ CH ₃ |

tion is translated into a preferred helix sense is non-bonded charge delocalization, as revealed by an analysis of structural data and theoretical calculations including a simple tertiary carbocation as a model system. The X-ray structures on which the analysis is based have been described before; however, it seems that no one has looked at them from the point of hyperconjugation.

In both **1a** and **2a**, the geminal methyl groups at C3 and C3' are diastereotopic as a result of the loss of molecular mirror symmetry: rotation of the end groups brings one of the two substituents into a more perpendicular orientation with respect to the chromophore and the other into a more in-plane position. For the former, the dihedral angle R–C3–C2–N1 is reduced from the perfect bisected value of 120°, and for the latter, it is enlarged. The X-ray data reveal subtle structural differences in the case of **1a** and rather drastic ones in the case of **2a**, where the two dihedrals differ by 28° and the corresponding bond lengths, C3–R¹ and C3–R², differ by 3.5 pm (Table 1). With one exception where the experimentally determined bond length appears rather peculiar (C3–R¹ in **1a**), it is the “perpendicular” methyl group, that displays the larger C–C bond length. This is, of course, also the group that is more prone to hyperconjugation with the twisted π -system of the chromophore.

Steric effects can be ruled out as an explanation because both groups extend away from the chromophore and the rest of the molecule. To rule out crystal packing effects as a possible cause for these differences, we have recalculated the structures using ab initio theory. Geometry optimization at the RHF 6-31G** level⁷ reproduces the experimental bonding situation (Table 1), not only with respect to the bond lengths but also with

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Table 2. Calculated Bond Lengths (in pm), Dihedral Angles (in deg), and Relative Energies (in kcal/mol) of Oppositely Twisted Cyanine Dyes **1b and **2b**^a**

| | C3–R ¹ | R ¹ –C3– C2–N1 | C3–R ² | R ² –C3– C2–N1 | rel energy |
|---------------|-------------------|------------------------------|-------------------|------------------------------|---------------|
| (M) 1b | 154.6 | –111 | 154.6 | 126 | 0 |
| (P) 1b | 154.1 | –120 | 155.1 | 117 | –0.9 |
| (P) 1b | <i>153.8</i> | <i>–127</i> | <i>154.5</i> | <i>111</i> | <i>–0.95</i> |
| (M) 2b | 155.5 | –100 | 154.2 | 138 | 0 |
| (P) 2b | 153.4 | –135 | 156.7 | 98 | –0.3 |

^aIn the P-helical forms, R² (the propyl group) is in the “perpendicular” orientation, and in the M-helical forms, it is in the “in-plane” orientation. Experimental data⁶ in italics.

respect to the dihedral angles, i.e., the relative orientation of the methyl groups and the chromophore.

If the peculiar pattern of bond lengths and dihedral angles of the geminal dimethyl groups in **1a** and **2a** is due to hyperconjugation, the nonracemic mixtures of **1b** and **2b** in solution should favor the diastereomer in which the group with the better hyperconjugative ability is in the more perpendicular position. Theoretical and experimental evidence shows that this is indeed the case. As before, we have performed RHF/6-31G** calculations on **1b** and **2b**, keeping C3 and C3' (*R*)-configured and optimizing the whole molecule starting with M- and P-helically twisted chromophores,⁸ respectively. (Table 2). Comparison of the diastereomers reveals the following. (i) In both dyes, the P-helical chromophore conformation in which the propyl group is in the perpendicular position is more stable than the inverted one in which the methyl group is in this place. The calculated energy differences are 0.9 and 0.3 kcal/mol for **1b** and **2b**, respectively. For **1b**, an energy difference of 0.9 kcal/mol has been determined experimentally.⁶ (ii) Regardless of the conformation, a small dihedral angle correlates with a long C–C bond. This is particularly apparent in the case of **2b**, where inversion of the helix sense from the less stable M- to the more stable P-helicity lowers the dihedral angle involving the propyl group from 138° to 98°, with a concomitant increase in the bond length of 2.5 pm; for the methyl group, the increase of the dihedral angle from –100° to –135° is accompanied by a bond shortening of 1.9 pm. (iii) In the one case where comparison with experimental data is possible (for (P)**1b**⁶), the agreement is good, though the structural differences are over-emphasized somewhat. The structure of the less stable (M)**1b** may be difficult to obtain experimentally because the two diastereomers equilibrate rapidly via an estimated barrier of only 12.5 kcal/mol.³

For a pictorial representation we refer to Figure 1, where part of **2b**, in the more stable P-helical conformation, has been plotted. The different orientations of the two alkyl groups with respect to the helix are quite obvious.

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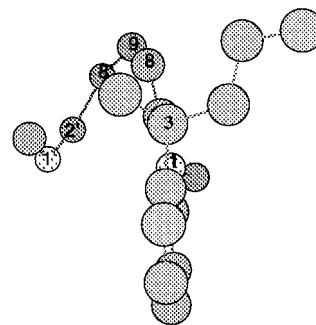
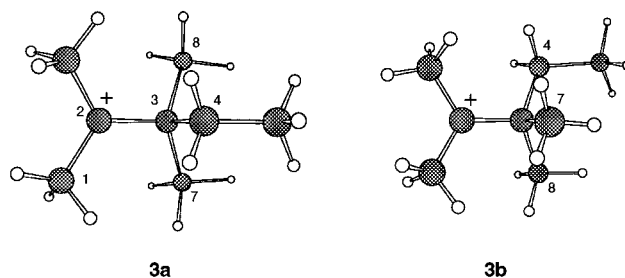


Figure 1. Part of calculated structure of (P)**2b**. The view is approximately along the C3–C2 bond; the helical chromophore is numbered. The methyl and propyl substituents extend from C3 to the left and to the right. The approximately perpendicular orientation of the latter with respect to the chromophore, which renders this the hyperconjugative group, is clearly seen. Hydrogens are omitted for clarity.

Both the methyl and the propyl group at C3 can interact with the positive charge at C2 by C–C hyperconjugation; the difference between the two substituents is their ability to stabilize the resulting positive charge as a methyl or as a propyl cation, respectively. To estimate the amount of stabilization that can be expected from this kind of interaction, we have calculated, as a model system, the structures and energies of two conformations of the 2,3,3-trimethyl-2-pentyl cation. In the starting geometry of **3a**, the C3–C4 bond was aligned parallel to the “vacant” p-orbital of C2, and in the other (**3b**), the positive center was rotated by 120°. The former



represents our model for C–C hyperconjugation by a propyl group (with the propyl group substituted by an ethyl group to save computational resources), and the latter, by a methyl group. The structures were energy-optimized at the restricted Hartree–Fock level of 6-31G** and also with density functional theory at the same level (B3LYP/6-31G**) to include the effect of electron correlation. Frequency calculations including zero-point energies were performed with the DFT geometries to ensure that minimum energy structures were found. Pertinent results are given in Table 3.

Both starting geometries lead to stable conformations, with deviations from perfect parallel alignment between the hyperconjugating C_α–C_β bond and the vacant p-orbital of from 3° to 8°. The observed bond lengthening due to hyperconjugation is somewhat larger for the ethyl group (3.8 pm according to RHF, 8.0 according to DFT) than for the methyl group (3.4 and 6.8 pm, respectively). The almost constant bond length of the second methyl group, whose orientation with respect to the positive center is comparable in both conformations, can be considered an internal point of reference for the two sets of calculations. With respect to relative energies, ethyl

Table 3. Relative Energies (kcal/mol) and Selected Bond Lengths (pm) and Bond and Dihedral Angles (deg)^a of the RHF- and DFT-Optimized Geometries of **3a and **3b****

| | RHF/6-31G** | | B3LYP/6-31G** | |
|---------------------------|-------------|-----------|---------------|-----------|
| | 3a | 3b | 3a | 3b |
| C1–C2–C3–C _{ecl} | –95.9 | –81.7 | –95.3 | –87.5 |
| C3–C4 | 159.0 | 155.2 | 163.7 | 153.3 |
| C3–C7 | 153.9 | 157.3 | 154.0 | 160.8 |
| C3–C8 | 154.4 | 154.3 | 154.6 | 154.3 |
| C2–C3–C _{ecl} | 99.7 | 100.6 | 96.9 | 97.0 |
| energy | 0.0 | 1.17 | 0.0 | 2.02 |
| ZPE | | | 145.3 | 145.2 |
| energy + ZPE | | | 0.0 | 1.92 |

^a C_{ecl} = C4 in **3a** and C7 in **3b**.

hyperconjugation is favored over methyl hyperconjugation by 1.2 (RHF) and 1.9 kcal/mol (DFT). The bias of the B3LYP method toward π -electron delocalization in the description of conjugated double bond systems has been noted before.⁹

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With the C2–C3–C_{ecl} bond angle close to or even less than 100°, both conformations display a strong tendency of the C _{α} –C _{β} bond toward bridging, a characteristic feature also of the hyperconjugating 2-methyl-2-butyl cation.¹⁰ In the cyanine dyes, the corresponding bond angles do not differ significantly from tetrahedral, a consequence of the rigidity imposed by the five-membered ring. This, in addition to the inability to achieve the optimum orientation with respect to the dihedral angle, explains why the calculated and experimental stabilization energies in **1b** and **2b**, which contain two of these differentiating centers, are significantly less than could be expected from the results of Table 3 alone.

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