Nonempirical Calculation of Polymethine Excited States**

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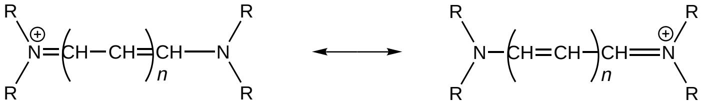
Polymethine dyes are charged or neutral, usually heterosubstituted, π-conjugated compounds in which the chromophore extends over an odd number of unsaturated centers.[1] As a consequence of this topological peculiarity, which restricts the perturbation of the π-electrons over the σ-skeleton, the electronic absorption bands of polymethines are narrow and intense and can be shifted by proper choice of the chromophore and substituents from the UV/Vis into the infrared (IR) region, which makes them by far the most important class of organic dyes.[2–4]

The theoretical treatment of polymethines, the industrial importance of which began with their use as spectral sensitizers in photography, has not improved significantly since Kuhn,[5] more than fifty years ago, and shortly thereafter Simpson,[6] treated the π-electrons of the simple streptocyanines (Scheme 1) quantum-mechanically as standing waves in a one-dimensional box of appropriate length. These calculations, which are extremely simple by today's standards, were nevertheless able to reproduce the nonconvergent behavior of the dyes, that is, the observation that each vinyl unit added to the chromophore produces a spectral shift of about 100 nm—a feat which modern quantum-mechanical methods have difficulties to achieve. Of these, the semiempirical Pariser-Parr-Pople (PPP) method has developed into the method of choice for correlating color and constitution of organic dye molecules, despite the only fair agreement between calculated and experimental absorption wavelengths.[7] Semiempirical schemes at the all-valence-electron level such as CNDO/S and ZINDO/S are also highly parameterized, and the results are useful for practical purposes but of limited theoretical value.



Scheme 1. Mesomeric formulae for polymethines considered, with $n = 0$–4 for $R = H$ and $n = 1$–4 for $R = CH_3$.

We are not aware of any calculations of polymethine excited states at the nonempirical level, which seems odd considering the recent interest these compounds as so-called functional dyes[8] for industrial use as laser dyes, in nonlinear optics, or as materials for optical data storage.[9] Herein, we report the quantitative agreement with experimental data of the excited-state energies of the simple streptocyanine dyes (Scheme 1, $R = H$ for $n = 0$ to 4, and $R = CH_3$ for $n = 1$ to 4) that we have calcultated using an ab initio multiconfigurational wavefunction combined with second-order perturbation theory (CASPT2).[10] The vinyl shift is quantitatively reproduced, as is the bathochromic shift arising from the methyl substitution at the terminal nitrogen atoms. The agreement with experiment is not the result of any arbitrary and serendipitous choice of the wave function, we have shown this by the systematic expansion of the basis set. Methods which employ single-determinant reference wave functions fail to predict correctly the excitation energies and the vinyl shift.[11] The calculations open the possibility of computing, at the ab initio level, the influence of electronic, geometric, and solvent effects on the spectroscopic properties of cyanine dyes.

Vertical excitation energies were based on ground-state equilibrium geometries which were optimized by density functional theory (DFT) using the B3LYP exchange correlation functional and the 6-31G** basis set.[12] The nonalternating bond lengths and the bond angles are scarcely affected by increasing the length of the chromophore; Figure 1 shows as a representative example, the optimized geometry of *N,N'*-tetramethylpentamethine. Along the chain there is a slight, but distinct alternation of the bond angles between around 121° and 125°, which correlates with the higher and lower π-densities at the respective carbon centers. Kulpe et al. have ascribed this alternation, which is clearly manifest in the X-ray structures of the streptocyanines,[13] to hybridization changes.[14] In agreement with this interpretation we find that the C–H bond lengths are longer at the carbon centers with higher s-character (i.e. larger C-C-C bond angles) and shorter at the carbon atoms between.

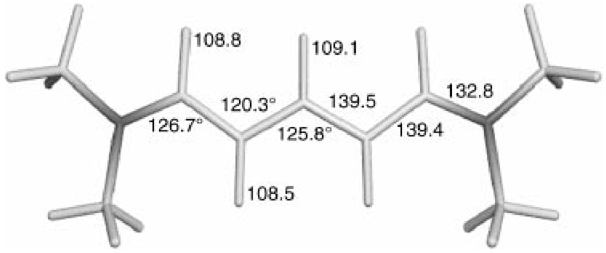


Figure 1. Energy-optimized B3LYP-6/31G** geometry of *N,N'*-tetramethylpentamethine, bond lengths [pm] and bond angles [°].

For the excited-state calculations we employed atomic natural orbital (ANO) type basis sets and the contraction scheme 4s3p1d/2s for the heavy atoms and for hydrogen, respectively. We also included, for the unsubstituted species, the more elaborate 4s3p2d/3s1p basis set. The active space for the CASSCF reference function included all π-orbitals (from 3 to 11) and π-electrons (from 4 to 12). State averaging was performed for the three lowest states considered. Energy corrections were calculated by CASPT2, and transition matrix elements by the CASSCF state interaction (CASSI) method, routines which are all provided within the MOLCAS-5[15] software package. In Table 1, the calculated energies of the first and the second excited states, S_1 and S_2, relative to the

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Table 1. Calculated[a] and experimental[b] energies[c] and (in parentheses) oscillator strengths of the two lowest polymethine excited states as a function of chromophore length and the substituents (Scheme 1).

R		$n=0$	1	2	3	4
H	S_1	6.5 (0.46)	4.28 (0.87)	3.18 (1.34)	2.52 (1.79)	2.11 (2.23)
H	exp.		4.34	3.28		
H	S_2	9.75 (0.15)	6.18 (0.05)	4.76 (–)[d]	3.68 (–)	3.01 (–)
CH_3	S_1		4.17 (0.74)	2.95 (1.16)	2.32 (1.81)	1.93 (2.29)
CH_3	exp.	5.53	3.99 (0.87)	2.98 (1.12)	2.39 (1.32)	1.98
CH_3	S_2		6.12 (0.03)	4.68 (–)	3.56 (–)	2.93 (–)
CH_3	exp.		5.71	5.51	4.00	3.45

[a] 4s3p2d/3s1p basis set for R = H and 4s3p1d/2s for R = CH_3. [b] Data are from B. Grimm, S. Dähne, G. Bach, *J. Prakt. Chem.* **1975**, *317*, 161 (R = H) and from S. S. Malhotra, M. C. Whiting, *J. Chem. Soc.* **1960**, *6*, 3812 (R = CH_3). [c] Relative to the S_0 ($^1A_1$) ground state; in eV. [d] Values smaller than 0.03 have been omitted.

ground state and their oscillator strengths are shown together with experimental results where available.

For the unsubstituted species, which were calculated with four different basis sets, only the results obtained with the 4s3p2d/3s1p basis are shown in Table 1. The energy of the $^1B_2$ state calculated with this (the largest) basis and with the smallest basis 3s2p/2s averaged over the five compounds differs by only 0.05 eV, that is, the results are practically independent of the basis set at this level of approximation. The energy difference of the higher $^1A_1$ state obtained with these two basis sets is significantly larger (0.34 eV).

The agreement of the S_1 state with the experimental data is excellent. The average deviation is 0.085 eV, which in the 500 nm range corresponds to about 17 nm. Moreover, the agreement is equally good for the short and for the long dye molecules and for the unsubstituted and the methyl substituted species, that is, both the vinyl shift and the bathochromic shift from the methyl groups are correctly reproduced. The agreement with the short axis polarized S_2 state is not quite as good (average deviation 0.55 eV) which is probably a result of experimental difficulties in localizing this weak transition next to the high-intensity S_1 state, but also to the higher calculation sophistication needed to describe higher excited states.

The bathochromic shift exerted by the methyl groups can be traced to a very simple pattern. Analysis of the wave function reveals that compared to the unsubstituted polymethines *all* the π-orbitals are raised in energy, but to a lesser extent as the orbital energies increase. This effect is exactly what one would expect from a perturbation of the π-orbitals of the chromophore by the low-lying p orbitals of each methyl carbon and the appropriate hydrogen 1s combinations, which leads to the decreased HOMO – LUMO gap and the observed red shift of the absorption maximum.

The calculated oscillator strengths of the S_1 state increase linearly with the length of the chromophore, in agreement with the simple electron in a box calculations. They agree closely with experiment for the short systems ($n = 1$ and 2). As the chromophore gets longer, there is a significant drop in the observed intensities relative to the calculated values, which may be an indication of the increasing contamination of the all-*trans*-polymethines by *cis*-isomers.

Configurationally, the S_1 state is quite pure consisting of 100 % of the HOMO – LUMO single excitation in the case of the monomethine; for the nonamethine, its proportion is still 78 %; the S_2 state always contains doubly excited configurations, the contribution reaching 37 % in the nonamethine.

With respect to their composition, the polymethine excited states resemble conjugated all-*trans*-polyenes, with the S_1 state corresponding to the optically allowed ^1B_u state and S_2 to the forbidden ^1A_g state.[16] However, in contrast to the polyenes, where the "dark" ^1A_g state drops below the ^1B_u state as the chromophore gets longer (the cross-over point appears to be reached with four conjugated double bonds[17]), the 2^1A_1 state stays significantly above the 1^1B_1 state, at least for the systems considered, though the gap decreases, from 1.9 to 0.9 eV, going from the tri- to the nonamethine. What happens to this gap as the chromophores become twisted or their symmetry is lowered by different end groups remains to be studied.

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