QUANTUM-CHEMICAL INVESTIGATION OF THE DISTRIBUTION
OF THE ELECTRON DENSITY IN ASYMMETRIC POLYMEThine
DYES

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It has been shown with the use of the HMO, PPP, and CNDO/2 approximations that the
distribution of the electron density in asymmetric polymethine dyes at the ends of
the polymethine chain is determined mainly by the electron-donor ability of the
nearby terminal groups, whereas in the middle their influence becomes weaker as the
chain becomes longer. The asymmetry of the dyes causes a decrease in the alterna-
tion of the charges on the atoms and an increase in the alternation of the bond
populations. These phenomena are most clearly displayed in the SCF approximations,
which always emphasize alternation. The closer are the electron-donor properties
of the terminal groups and the longer is the polymethine chain, the smaller is the
difference in the distribution of the electron density near the terminal residues
in asymmetric and symmetric dyes.

Asymmetric polymethine dyes have aroused increased practical interest owing to a number
of spectroscopic peculiarities of these compounds [1]. In the present work we have ascer-
tained the laws governing the distribution of the electron density in asymmetric polymethine
dyes as a function of the length of the polymethine chain and the electronic nature of the
terminal groups, i.e., their effective length L and their electron-donor ability ϕo [2].

Model dyes with the general structure

\[ \text{[} \text{X} \text{-(CH=CH)\text{H}} \text{CH-Y\text{]}} \]

were studied by the HMO, PPP, and CNDO/2 methods. The terminal groups were considered in the
CNDO/2 approximation in order of increasing electron-donor abilities, i.e., CH2=CH, NH2, SH,
OH, O-. The vinylogous series (n = 1 to 7) were constructed in such a manner that \( \phi_{OX} > \phi_{OY} \).
A geometry of the polymethine dyes with equal bond lengths was used in the calculations.
Optimized geometric parameters were also obtained with the aid of the program in [3] for the

![Fig. 1. Bond angles and lengths in polymethines \( n = 2 \)
(a), \( n = 3 \) (b) and merocyanines (c) optimized in the
CNDO/2 approximation.](image-url)
polymethines ($X = Y = CH_2CH$) and the merocyanines ($X = CH_2CH, Y = O^-$) (Fig. 1). In this case, the changes in the charges of the atoms did not exceed 0.05, and the changes in the bond populations did not exceed 0.09 au.

The alternation of the charges in the asymmetric polymethine dyes, as in the symmetric dyes [4], decreases as the length of the polymethine chain is increased, and for a specific polymethine chain it decreases as the difference between the electron-donor abilities of terminal groups $\Delta \delta = \Phi_{XY}$ is increased, the alteration on the edges of the chain being greater than in the middle (see Fig. 2 and Table 1). This is consistent with the experimental data, particularly with the differences between the values of the chemical shifts $\delta^{(1)} C$ in the NMR spectra [5].

For example, when $n = 3$, for the merocyanines $[X = N(CH_3)_2, Y = O^-]$ $\delta_M - \delta_{M-1} = -38.0$ ppm, $\delta_{M+1} - \delta_M - \delta_{M-1} = 29.5$ ppm, $\delta_{M-1} - \delta_{M-2} = 32.1$ ppm, and $\delta_{M+2} - \delta_{M+1} = 48.6$ ppm; in the cyanines $[X = Y = N(CH_3)_2]$ $\delta_M - \delta_{M-1} = -41.4$ ppm, and $\delta_{M-1} - \delta_{M-2} = 54.7$ ppm; in the oxonols ($X = Y = 0$) $\delta_M - \delta_{M-1} = -49.6$ ppm, and $\delta_{M-1} - \delta_{M-2} = 46.0$ ppm ($M$ is the index of the atom in the meso position) [5]. When the geometry is optimized, the alternation of the charges in the polymethines is enhanced, while in the merocyanines it is smoothed, and thus consideration of the vibronic coupling emphasizes the laws discovered with the use of the geometry with equal bond lengths.

In the asymmetric polymethine dyes the charges on atoms which are equidistant from the center of the polymethine chain are different, i.e., they are greater on the atoms located closer to the more electron-donor terminal group, for example, $O^-$ [5]. This peculiarity can be revealed only with the aid of calculations in the CNDO/2 approximation with an optimized geometry.

As is seen from Table 1, the atomic charges at the ends of the polymethine chains in the asymmetric polymethine dyes are determined mainly by the nearby terminal group. The influence of the distant terminal group must be taken into account, if the difference between their electron-donor abilities $\Delta \delta$ is significant. In both the asymmetric and symmetric dyes the terminal groups transfer more charge to the polymethine chain, the greater is their electron-donor ability. For example, when $n = 7$, the charge of the polymethine chain is almost linearly dependent on the sum of the electron-donor abilities of the terminal groups in the asymmetric polymethine dye.

In the framework of the approximation of dyes with a very long polymethine chain [2], the change in the electron density on the p-th atom upon the transition of the molecule of a polymethine dye to the first excited state ($\Delta_{pp}$) is written in the form

$$
\Delta_{pp} = (-1)^{p+\rho+1} \cos \left( \frac{\rho}{n+L} (\Phi_{OX} + \Phi_{OV} - \pi/2) + \Phi_{OX} - \Phi_{OV} \right) \cos \frac{\rho \pi}{2(n+L)}
$$

**Fig. 2.** Charges on atoms of polymethine chains calculated in the HMO approximation in symmetric (dashed lines) and asymmetric (solid lines) polymethine dyes: a) $\alpha_X = \alpha, \alpha_Y = \alpha 2\beta, \Delta \phi = 63.5\degree$; b) $\alpha_X = \alpha + 1.5\beta, \alpha_Y = \alpha + 2\beta, \Delta \phi = 26.6\degree$; $N$ is the number of the atom.