8 Computer-assisted dyestuff design and synthesis

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8.1 Introduction

Dye chemistry, often called the mother of organic synthetic chemistry, may also be referred to as the father of modern theoretical chemistry. Well after Perkin had discovered the first synthetic dye, Mauveine, in 1856, Witt developed his chromophore theory in 1876, which was then reformulated in the 1920s by Dilthey and Wizinger. Other important contributions were made by Willstätter (meriquinoid principle in 1908) and König, who based his assumption on knowledge available in 1926 of all dyes having a polymethine structure. The early 1930s saw the dawn of modern quantum-chemical theory which, however, only began to manifest an enormous impact on our understanding of organic chemistry in general, and on the chemistry and physics of $\pi$ systems in particular, after the development of high speed computers in the second half of this century.

Within the last few years, computer programs have been developed which are not based on quantum-chemical but force-field methods, allowing for fast calculations of the molecular geometry and dynamics of single molecules as well as more complex systems.

In retrospect, one may gain the impression that the availability of quantum-chemical and force-field tools has been lagging behind the experimentally acquired knowledge base. However, an analysis of recent publications, especially in the area of pharmaceutical chemistry, reveals an increasing application of molecular modelling programs prior to experimental work. In the field of fibre-dye chemistry, on the other hand, theoretical methods have been, up to now, primarily used for the explanation, rather than the prediction of, certain properties, which may be ascribed to the fact that in these cases, applicatory rather than spectroscopic or structural properties are of importance. Nevertheless, on special dye systems such as near-infrared dyes, dyes with various chromotropic properties, dyes for pigments, nonlinear optics, liquid crystals, and lasers, and even colourless “dyes” as optical brighteners, theoretical calculations are increasingly being carried out first, in order to minimize experimental efforts.

This chapter is designed to provide a survey of the commonly used theoretical methods in dye chemistry, to discuss their scope and limitations, and to present some examples as illustrations of their advantages. Speculation is also made on the direction of future developments in theoretical chemistry. The methods discussed will be restricted to the quantum-chemical area for two reasons: first, con-
sidering dye design, colour, as the essential physical expression of a dye, can only effectively be calculated by these techniques; and second, reflecting on synthetic aspects, reference to methods such as search and retrieval of dye syntheses in public data banks are beyond the scope of this chapter. Therefore, the coverage will be limited to aspects such as reactivity and selectivity of dyes and their intermediates. Methods such as force-field procedures may, in the future, contribute to areas where the colour of a dye is not only assumed to be affected by its molecular geometry (which in most quantum-theoretical calculations is merely an input quantity) but also where its immediate surroundings must be considered (e.g. solute-solvent interaction, crystal structure in pigments) and therefore optimized, or where applicatory properties (e.g. fibre dyeing) are of importance.

8.2 Quantum-theoretical methods: scope and limitations

It is well known that a great variety of quantum-chemical methods exists, which are all related to the same quantum-theoretical approach, viz. the linear combination of atomic orbitals (LCAO) procedure (except for the free-electron molecular orbital [FEMO] method, which is useful only in the special case of linear molecules). These methods are principally separable into one-electron and multi-electron procedures, the latter being further divided into semiempirical and nonempirical, ab-initio, procedures, which differ greatly in their complexity, accuracy and computation time. The selection of the appropriate calculation procedure therefore, merely depends on the question which is being addressed. In this review, only those methods which have found wide applicability in the calculation of larger \( \pi \) systems, i.e. the HMO and semiempirical methods, will be described.

8.2.1 HMO method

The most elementary method based on the LCAO procedure, i.e., the one-electron approximation called the Hückel-Molecular Orbital (HMO) method, makes use of the \( \sigma-\pi \) separation principle. This has its merits in that for a given planar \( \pi \) system, the eigenvalues and eigenvectors of which are calculated extremely fast, qualitative predictions about absorption-spectral changes and relative chemical selectivities can readily be made, based on the useful extension of the HMO theory, the perturbational molecular orbital (PMO) theory. On this quick and simple basis, even the dependence of the thermodynamic equilibria of the tautomeric forms of a series of \( \alpha \)-hydroxyazo and \( \alpha \)-aminoazo dyes on the substitution patterns has been reliably rationalized. This may be helpful in designing new analogous dyes in view of the fact that the colour of these dye systems is highly influenced by the position of this equilibrium. An illustrative example is outlined below, since it demonstrates particularly well the power of the combination of HMO and PMO theory.