

Organic Photochromes

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Organic Photochromes

PREFACE

Only a small part of the numerous photochemical reactions in organic compounds result in reversible structural changes. The latter are accompanied by a change in physical properties, in particular, of electronic spectra. It is tempting to try to use this photochromic effect in various systems for controlling and regulating light fluxes and for data recording. Eventually an independent trend emerged in photochemistry – the study of the photochromism of organic compounds to establish relationships between structure and photochemical behavior, the theoretical analysis of these relationships to predict structures with pre-set photochromic parameters, and, finally, the identification of suitable areas for the application of photochromism. This monograph summarizes the results of recent studies carried out by a number of research institutions in the USSR and the GDR. Devoted to an important aspect of applied photochemistry, this monograph contains a detailed exposition of the chemical photochromes referred to briefly in the earlier editions of "Introduction to the Photochemistry of Organic Compounds" (Khimiya Press, Moscow, 1976) and "Photochemical Processes in Layers" (Khimiya Press, Moscow, 1978).

In Chapter 1 we point out that the theoretical elaboration of the problems of photochromism relies on a wide variety of concepts, and that analysis of changes in the potential energy surfaces of photochromic systems during reaction appears to be the most promising method of research. Whereas Chapters 2 and 3 deal with traditional photochromic systems, Chapters 4 and 5 describe the excellent prospects for the synthesis of photochromes from a series of potential tautomers. Chapter 4 also contains a section on aryloxyquinones written by Yu. E. Gerasimenko of the Scientific-Research Institute of Organic Intermediates and Dyes, Moscow, and a section on acylo-tropic regroupings written by V. I. Minkin, G. D. Palui, V. A. Bren, and A. E. Lyubarskaya of the Scientific-Research Institute of Physical Organic Chemistry, Rostov-on-don, RSFSR. The possibility of using photochromes for accumulating and storing solar energy through the energy of chemical bonds is of special interest in this context. Chapter 6 contains a brief survey of the entire body of available data on the so-called luminescent photochromes, which can be used to increase sharply the sensitivity of photochromic systems.

A. V. El'tsov

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Chapter 1

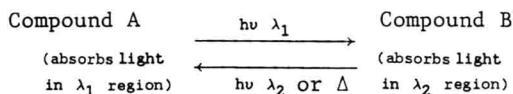
THEORETICAL STUDIES OF THE PHOTOCHROMISM OF ORGANIC COMPOUNDS

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Photochromism, one of the more striking phenomena of photochemistry [1-4], is the transition between two chemical compounds*** A and B with markedly different absorption or emission (see Chapter 5) spectra induced in at least one direction by electromagnetic radiation:



Changes in light absorption and luminescence always entail an abrupt alteration of the chromophore system: in the case of chemical photochromes the $A \rightleftharpoons B$ transitions usually result in substantial molecular restructuring.

Photochromic systems are distinguished by the following:

- a) Structural changes are reversible. Transition to metastable compounds are photochemically induced from thermodynamically stable compounds.
- b) Associated with structural changes $A \rightleftharpoons B$ is a change in physical and chemical properties, of which color change is, at present, of the greatest scientific and practical interest.
- c) Depending on the properties of photochromic systems, forward and reverse reactions may proceed through electronically excited singlet or triplet states. Metastable form B may have a lifetime of from a few microseconds to hours, days, or weeks. This factor is of decisive importance for potential practical uses of photochromic systems [5,6].
- d) Photochromic systems are often also thermochromic; i.e., reversible changes in them proceed thermally. In many cases the back reaction in photochromic systems is also induced thermally.

***We are not concerned here with physical photochromes whose photoinduced coloration is due to the light absorption of the resulting excited atoms, molecules, and ions.

e) In theory the forward and reverse reactions can be repeated indefinitely. Real photochromic systems show signs of "aging"; the number of conversion cycles from A to B and back into A decreases on account of side reactions. The practically achieved number of cycles ranges from 1 to about 10^6 .

Most photochromic systems are based on bond cleavage, isomerization, or oxidation-reduction reactions.

Bond cleavage proceeds either homo- or heterolytically. Thermal recombination of the radicals in the reverse reaction corresponds to homolytic bond cleavage. The light energy necessary for homolysis corresponds to the energy of dissociation of the bond being split. The relative stability of the resultant radicals is heavily dependent on the electronic structure of the given compound (for instance, "mesomer stability" through delocalization of the unpaired electron is possible). C-C bonds (for instance, in bistetraarylimidazoles), as well as C-N bonds (in hexaarylbisimidazoles), N-N bonds (in nitroso dimers), and S-S bonds (in diaryl disulfides), are homolytically broken.

Heterolytic bond cleavage and, accordingly, thermal recombination of resultant ions in the back reaction are to be found particularly frequently in photochromes whose structural and electronic factors favor the formation of relatively stable ionic or intraionoid reaction products; the latter have structural elements of polymethines noted for their deep color (for instance, triarylmethyl cations, merocyanines).

The characteristic differences, especially in physical properties, between E- and Z-isomers as well as the easy course and often considerable quantum yields of photochemical isomerization enable us to regard many classes of unsaturated compounds as potential photochromic systems. Here the difference between the positions of the absorption bands of E- and Z-isomers in certain groups of compounds is found to be in excess of 100 nm. Generally, because of the longer transition moment, the E-form absorbs more intensely than the Z-form; the E-form is thermodynamically more stable (see Chapters 2 and 3).

Stilbenes, polymethines, indigoids, azomethines, azo compounds, azines, triazenes, and other compounds exhibit pronounced photochromism due to E- and Z-isomerization. In some photochromic systems E-, Z-isomerizations precede another photochromic process (for instance, stilbene photocyclization) or follow it (for instance, ring opening in spiropyrans).

Photoinduced valence tautomerism is another example of photoisomerization. It takes place when as a result of a rearranged electronic structure (which may change the bond lengths and angles but which does not substantially affect the relative steric position of atoms and atomic groups) equilibrium is reached between valence isomers [7]. This tautomerism includes: a) intramolecular ring opening (as, for instance, in spiropyrans; 2H-pyrans and -thiopyrans; 2H-chromenes and -thiochromenes, dihydroxanthenes; trans-10b,10c-dialkyldihydropyrenes); b) intramolecular cyclization (for instance, in 1,3,5-hexatrienes, fulgides, stilbenes, bianthrone, nitrones, 1,3-butadienes, and others). Intermolecular cyclodimerization is described in the series of pyrimidine bases, coumarins, carbostyryls, 1,4-naphthoquinones and other quinones, and anthracene and acridinium derivatives.

In most cases light-induced reversible hydrogen transfer leads from thermodynamically stable ortho-substituted aromatic structures to colored compounds with a quinoid structure through a six-membered transition state. Typical groups of such compounds include, in the case of keto-enol tautom-

erism, quinolones, alkylbenzophenones, arylimines, o-hydroxyaldehydes, o-hydroxyarylalazines, -aryl azo compounds, benzophenones, and salicylates; in the case of acinitro tautomerism - o-nitrobenzene compounds; and in the case of hydrogen transfers in metal-complex compounds - metal dithizonates.

Photochromic reduction-oxidation systems are distinguished by a light-induced reversible electron transfer between the donor and the acceptor, which are found in at least two stable redox states. Examples of such reduction-oxidation systems include cell chlorophyll, the thiazine dye-Fe(II) or Sn(II), 3,6-dichlorofluorene-dye-disulphydryl complex, as well as derivatives of p-phenylenediamine and triphenylamine in combination with the corresponding matrices in which reversible photoionization occurs.

The aim of theoretical and quantum-chemical studies of organic photochromic systems is to elucidate the following points:*

- 1) to estimate the energy levels of the ground and electronically excited states of all the particles involved in the photochromic process;
- 2) to characterize the absorption spectra of all the particles, i.e., to calculate the positions of absorption maxima, to ascertain the nature of electron transitions, and to assess their intensity and polarization direction;
- 3) to quantify the photochemical activity of photochromic molecules;
- 4) to describe the mechanisms of photochromic reactions and to estimate thermodynamic parameters characterizing the reaction (activation energies, activation enthalpy, entropy effects);
- 5) to elucidate the chemical structure of the compounds participating in the photochromic process with the aid of thermodynamic values, spectroscopic data, and parameters of electronic structure;
- 6) to find a connection between the structure and chemical behavior of compounds with a view to developing photochromic systems which would have optimal parameters from the standpoint of their practical application.

No methodologies described in the literature assure equally successful solutions to the above-stated questions for all potential photochromic systems. This reflects the state of the art of contemporary theoretical chemistry, in general, and of photochemistry and quantum chemistry, in particular. Therefore, workers in the field have been looking at individual problems in accordance with their importance for each specific photochromic system. The quality of the results of these efforts varies since they employ different theoretical approaches to the problems of photochemistry [8-10].

1. The use of qualitative models and correlation graphs:

a) the classification and description of synchronous photochemical reactions with the help of the Woodward-Hoffmann rules [11], the Fukui concept of frontier orbitals [12,13], the Hückel-Mobius concept as modified by Zimmerman [14], Dewar's ideas on the aromatic and anti-aromatic transition states [15,16], graph theory [17];

*Naturally, attempts at solving the scientific tasks in the field of photochromes mentioned here and elsewhere can produce good results, given a favorable combination of theoretical approaches with the experimental techniques of photochemistry.

- b) qualitative description of synchronous polar cycloaddition with the help of diagrams of the donor-acceptor interaction of cycloadducts [18,19];
- c) estimating molecular interaction energies with the help of perturbation theory to determine their capacity for entering into photocycloaddition [16];
- d) qualitative assessment of the shape of potential curves along the coordinate of the reaction for certain photoreactions with the help of correlation diagrams of state; systematization of types of photochemical processes [20-22];
- e) estimating the geometry and energy of photochemical intermediates in various electronically excited states to develop hypotheses about the reaction course and to identify its special features such as stereospecificity [8,23].

2. Calculating spectrophysical characteristics of photochromic compounds: their absorption, luminescence, radiationless deactivation, the efficiency of intramolecular energy transfer, etc.

3. The use of statistical and dynamic indices of the reacting components for describing the electronic structure of electronically excited Franck-Condon states and for developing ideas on the reactivity of molecules in photochemical reactions [9].

4. Calculating potential energy curves and surfaces or parts thereof for the ground and electronically excited states of molecules. These data, along with information about the geometry of various excited states, often provide more detailed information on the course of the reaction, the thermodynamic characteristics of the starting materials, intermediates, and reaction products, as well as on spectrophysical parameters [24-27].

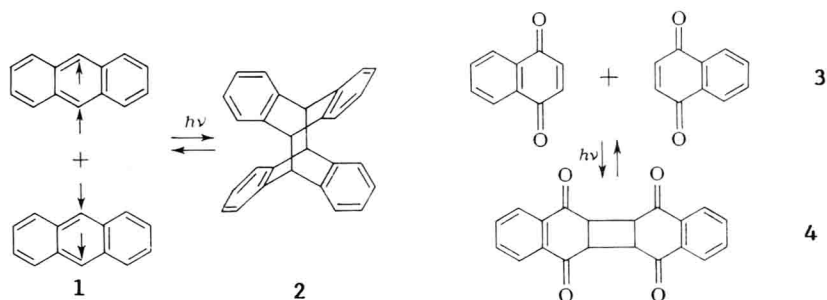
In view of the great variety of theoretical concepts found in the literature, the varying standard of research, and in the absence of summarizing, comprehensive methodologies we have grouped the main theoretical works on organic photochromism by research method and photochrome group.

While the use of qualitative models for the photochromes has yielded relatively modest results, the quantum-chemical calculations of the spectra of photochromic system components and the indices of their reactivity have made it possible to find important correlations between structure and properties for practically all groups of organic photochromic systems and to assess the structure of photoinduced forms. The results of the calculations of potential energy surfaces are presented in a special section.

THE USE OF QUALITATIVE MODELS AND THE WOODWARD-HOFFMANN RULES FOR DESCRIBING PHOTOCHROMIC SYSTEMS

The ideas of Woodward and Hoffmann [11] are normally drawn upon in classifying and describing in qualitative terms synchronous photochemical reactions such as cycloaddition and ring opening, electrocyclic and chelotropic reactions, group transfer, sigmatropic regroupings, and elimination. Of these only cycloaddition, ring opening, and electrocyclic reactions have by now been realized in photochromic systems.

The Woodward-Hoffmann rules provide the first basic idea of the steric course of photochemical reactions. $[4 + 4]$ -Cycloaddition occurs during the cyclization of anthracene 1 and acridizinium derivatives and certain pyridine bases. In the case of coumarin compounds and 1,4-naphthoquinone 3, $[2 + 2]$ -cycloaddition is realized:



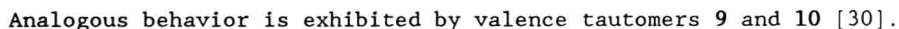
In accordance with the Woodward-Hoffmann rules, these reactions are photochemically allowed if cycloaddition takes place from the same side of the reacting parts of both molecules (supra,supra-cycloaddition). Qualitative conclusions regarding the possibility of a reaction occurring are drawn from an analysis of correlation diagrams. For instance, one worker ([11], see Figure 10) presents a simplified correlation diagram of electronic states for a model of $[2 + 2]$ -cycloaddition: 2 Ethylene = Cyclobutane. The lowest excited state of both ethylene molecules corresponds to the electronic configuration $(SS)^2(SA)^1(AS)^1$; the bonding and antibonding molecular orbitals are symmetric with respect to two surfaces (σ_1 divides the C=C bond, σ_2 is parallel to both molecular surfaces and is equidistant from both). This excited state has the same symmetry as the first excited state of the reaction product - cyclobutane. This means that the symmetry of these states does not change as a result of the reaction and both states directly correlate and the reaction is symmetry-allowed.

It is impossible to obtain more detailed information from such correlation diagrams on potential curves or potential surfaces, the less so since this approach does not distinguish the spin multiplicity of reacting excited states.

Electrocyclic reactions, in keeping with the Woodward-Hoffmann rules, follow a strictly stereospecific course, either disrotatory in the excited state of diene structural fragments or conrotatory in the case of trienic structures. As a result, the substituents at the extreme ends of the dienic systems in the cyclobutane reaction product are in a cis-position relative to each other, while in the cyclic products derived from hexatrienic structures they are in a trans-position. Accordingly, hydrogen atoms in the product of stilbene cyclization - 4a,4b-dihydrophenanthrene - must be in the trans-position [28]. So far, no experimental proof of this fact has been obtained. In the case of 1,2-diphenylcyclopentene 5 the Z-structure was originally recorded since its molecule is a convenient model for studying reversible photocyclization uncomplicated by E/Z double-bond isomerization.



Compounds 7 and 8 form a relatively stable system among the photochromes of this class; colorless 1,1',3,3',5,5'-hexamethylstilbene 7 on ultraviolet irradiation is converted into red-colored hexamethyldihydrophenanthrene 8. The latter is not oxidized into a corresponding phenanthrene derivative, but it easily opens the ring in the back reaction [29].

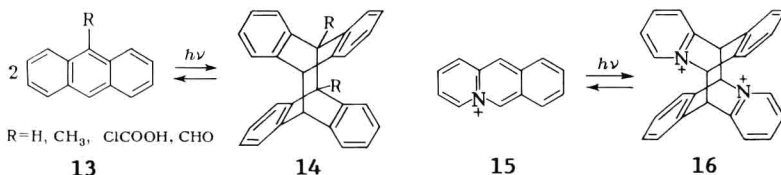


Chemical reaction scheme showing the photochemical [2+2] cycloaddition of two molecules of 2-benzofuranone (11) to form a dimer (12). The reaction is reversible and initiated by light ($h\nu$). The dimer 12 is specifically the "head-to-head endo-adduct".

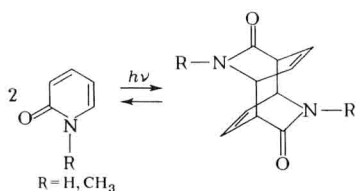
Of the binding interactions, the stronger ones (\searrow) lead to the formation of a covalent bond while the weaker ones (\swarrow) determine the regioselectivity of the reaction. It then becomes clear why coumarin dimerization through the singlet state results in the formation of an endo-adduct of the "head-to-head" type exclusively. If the reaction proceeds through the triplet state, both endo- and exo-products of "head-to-head" cycloaddition are formed along with traces of the "head-to-tail" type of product [31]. According to other workers [8,23], these differences in reaction stereospecificity depending on the multiplicity of reacting excited states may be due to differences in the geometry of the reacting particles, which, in turn, is attributable to a different electronic structure.

Assessment of the geometry of singlet and triplet intermediates with due allowance for spin and electron-electron repulsion shows that in biradicaloid triplet states the electronic cloud is loose; this accounts for the tendency of such systems towards the separation of the resultant radical pairs, geometrical isomerization, and the loss of reaction stereospecificity.

Photodimerization of 9-substituted anthracenes **13** leads in most cases to "head-to-head" dimers.



Conversely, in the analogous reaction of acridizinium 15 and pyridine 17 compounds, cycloadducts of the "head-to-tail" type are formed for the most part - 16 and 18, respectively.



17

18

On the basis of perturbation theory we can easily draw reliable conclusions regarding the nature of the excited state involved in intermolecular cycloaddition [12,13,16,32-34].

Salem [34] has proposed a useful method fairly readily applicable to reactions involving large π -electronic systems which, quickly and without complex calculations, can help to evaluate in qualitative terms the structure of the potential surface in the π -electronic approximation as well as the reaction path for conjugated reagents that are not too strongly polar. Unfortunately, no data have yet been reported on the application of this method to photochromic systems.

QUANTUM-CHEMICAL CALCULATIONS OF THE SPECTRA OF PHOTOCHROMIC SYSTEM COMPONENTS AND STATISTICAL AND DYNAMIC INDICES FOR ESTIMATING THEIR REACTIVITY

Knowledge of the energetic position of the ground and reactive electronically excited states (S_1 , T_1) as well as of spectroscopic data (the position of the absorption maximum in the electronic spectrum, the absorption intensity and the direction of electronic transition polarization), and the connection between light absorption, the type of corresponding electronic transfers, and the molecular structure of photochromes is a fundamental factor in work on problems of photochromism, including for optimization of such systems for the purpose of their practical application. Quantum-chemical techniques have found useful applications for the solution of these problems along with experimental measurement techniques which have been greatly improved over the past two decades (emission spectroscopy, spectroscopic techniques for the study of fast reactions).

Given certain prerequisites (for instance, during consideration of narrow groups of compounds, general directions of conversion), it is possible to draw simple qualitative conclusions about the spectra of photo-induced forms even using the most elementary quantum-chemical approaches (for instance, the Hückel method). A good semiempirical method for calculating the spectral data of electronic systems (such as the SCF PPP CI method) makes it possible (given optimum parametrization) to obtain results which are in agreement with experimental ones within the measurement error (for instance, during the determination of the position of the absorption maximum); however, the band intensities in the spectra are, in most cases, overstated. By means of a special parametrization [35] it is possible to estimate with a high degree of accuracy the $S \rightarrow T$ transfer energies as well; bearing in mind the existence of additional centers of special parametrization we can also describe the $n \rightarrow \pi^*$ -electron transfers [36]. To describe the electronic spectra of nonconjugated compounds and systems with delocalized π -bonds, a modification of the CNDO method with special parametrization (the CNDO/S variant) [37,38] is used. However, the lengthy procedure involved, as compared with the method in the π -electronic approximation, does not offer substantial advantages for calculating $\pi \rightarrow \pi^*$ -transitions. Some of the electron transfers ($\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$) can be characterized with the aid of wavefunctions of the electronic states between which the electronic transition occurs.

In many cases certain conclusions can be drawn from an analysis of the configuration interactions regarding the photochemical reactivity of electronic states as well as about its connection with structure [39,40].

In many photochromic systems, the lifetimes of the photoinduced form are brief and cannot be determined, and they can only be identified by electronic spectra. The latter are calculated for a number of possible structures. The most probable structure (or structures) can be chosen on the basis of the calculations, and its (their) parameters are correlated with the experimental data.

Modern quantum-chemical methods involving different levels of expenditure and varying degrees of accuracy can be used to calculate the most stable structure and geometry of molecules in the ground state (the geometry optimization technique) [41,42] and in the excited state [43,44]. By comparison, experimental techniques for determining the geometry of molecules in excited states are extremely complex and are applicable to only some of the systems [45].

Knowledge of the structure of the ground and excited states of photochromic system components provides useful information on the paths of reversible photoreactions, on the mechanisms of side processes, on the influence of environments differing in nature (viscosity and other parameters), and on the state of photochromic equilibria. For instance, general rules have been created for cyclic alternant and nonalternant hydrocarbons [46] which help draw conclusions regarding the geometry of energetically favorable structures in the ground and excited S_1 - and T_1 -states.

Static and dynamic indices of reactivity for electronically excited states can be calculated by a similar technique used in the case of the corresponding values for the ground state. The static values used include charge density, bond orders [47], electronic populations of bonds [48], and free valences [47,49]. With the help of these values one can characterize in crude terms the electronic structure of a molecule in its electronically excited state. The dynamic indices of reactivity include relative changes in bond energy on electronic excitation [50] and in localization energy [28, 51]. The use of reactivity indices assumes that a conclusion regarding the preference of the molecule for a given photochemical reaction can only be drawn from an analysis of the parameters characterizing its electronic structure in the Franck-Condon state (static indices) or that this tendency can be evaluated on the basis of changes in electronic energy during the molecule's crossing from the Franck-Condon state to the transition state. A note of caution should be sounded here against an uncritical use of such values.

Above all, the numerical values for such estimates are arrived at within the framework of simple one-electron models (for instance, by the simple Hückel method), which give no satisfactory description of either the character of excited singlet states or the differences between the singlet and triplet states. Strictly speaking, such indices of reactivity can only be used for reactions which proceed adiabatically or when the rate is limited by the primary photochemical processes.

In many cases such an analysis fails to produce absolute values, and workers often confine themselves to qualitative or semiquantitative conclusions regarding the relative change in reactivity of large series of structurally related compounds. A description of the major approximate operations and of their application to the solution of problems of reactivity is contained in the papers [37,52], while a detailed exposition of photochemical reactivity is given in the paper [9].

The photolysis of practically colorless spiropyrans involves the cleavage of the carbon-oxygen bond of the pyran ring and the formation of a merocyanine dye. Spiropyran molecules are composed of two topologically orthogonal parts linked by a sp^3 -hybridized carbon spiroatom. For indoline spiropyrans [53], intramolecular energy transfer from the indoline to the pyran portion (or in the reverse direction, depending on structure-energy correlations) is highly probable. Indirect evidence of this is supplied by luminescent measurements [54]. It has been theoretically proven [55-57] that because of the slight overlap of p-atomic orbitals next to the spiro-carbon ones, along with an electrostatic interaction, an exchange interaction takes place. This effect, denoted as spiroconjugation, is reflected in the changes of the electronic spectra of formally isolated molecular halves of the spiro compounds. For spiro compounds possessing a relatively high symmetry (such as spirodifluorenes with D_{2d} symmetry), interaction is symmetry-forbidden. Compounds with a lower symmetry do not obey such selection rules, and this is what we should expect from the majority of photochromic spiropyrans.

The absorption and luminescence spectra of the spiropyrans were first studied using one group of compounds as a prototype [54,58]. The spectra of indoline spiropyrans were compared with those of substituted chromenes and indolines, and the influence of the substituents on electron transfers was analyzed to establish a series of dependences between structure and spectral characteristics. The electron transfers relating in the spectrum to particular bands are localized in different parts of the molecule. The first (a band of some 320 nm) and third (about 260 nm) electron transfers are localized in the chromene part. Luminescent measurements showed that the lowest singlet or triplet states have a π, π^* -character. The lowest triplet state has an n, π^* -character only, given the presence of nitro groups in the chromene part. The second (290-300 nm) and fourth (about 240 nm) spiropyran transfers were located in the indoline part. Quantum-chemical calculations by the CNDO/S method confirm, at least qualitatively, this relationship of the bands in the spectrum [59].

To assess the intramolecular energy transfer [60] in the case of spirodifluorenes, Förster's theoretical concepts [61] were used.

The PPP method was used for numerical calculations of the wavefunctions of the partially isolated chromophores of the a and b parts of the molecule (Figure 1) [62]. The configuration interaction (CI) coefficients calculated by this method are used to evaluate the interaction integrals. For asymmetrically substituted spirodifluorenes, values of the interaction integral

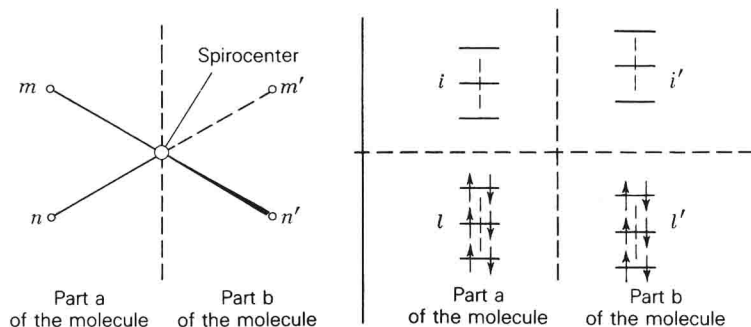


Fig. 1. The plot of the a and b portions of the spirodifluorene molecule interacting through the MO spiroatom.