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Intramolecular Charge Transfer, Studied by Electrochromism of Organic Molecules in Polymer Matrices

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The ground state dipole moment, $\vec{\mu}_0$, and the change in dipole moment upon excitation, $\overrightarrow{\Delta\mu}$, of various dyes have been determined from electrochromic measurements on solutions in polymer matrices. The merits of this method are discussed. High values of $|\vec{\mu}_0|$, much in excess of the sum of local group moments, are found for compounds in which a polar ground state is stabilized by large differences in electronegativity of the constituting groups ("Zwitterions") and/or by a gain in resonance energy accompanying a charge transfer in π-electron ring systems. High values of $|\overrightarrow{\Delta\mu}|$, indicating a large charge transfer upon excitation, are connected with a loss of resonance energy. The amount of charge, transferred upon excitation from the donor group of the dye to the acceptor group, does not decrease significantly if the geometric distance between these groups is increased by inserting enthynylenic groups.

INTRODUCTION

The electric dipole moment of molecules in the ground state, $\vec{\mu}_0$, as well as that in the excited state, $\vec{\mu}_1$, may be measured with the help of electrochromic effects, *i.e.* variations in the absorption or emission spectra, induced by applied electric fields. Two different physical processes contribute to electrochromism. First, molecules having an electric dipole moment and/or an anisotropic polarizability will change their orientation under the influence of an electric field. Secondly, a field will perturb the molecular wave function, resulting in shifts of energy levels and changes in transition moments. If the difference in anisotropic polarizabilities of ground state and excited state is not considered, the shift in energy levels is directly proportional to the difference between the dipole moment of both states. Such a difference reflects the charge transfer accompanying the electronic transition.

Electrochromism is usually measured on liquid solutions, where both processes mentioned above occur simultaneously. We have studied electrochromic effects of some organic dyes dissolved in polymer matrices. Although a few measurements of this type have been published before,[1] the full merits of the method do not seem to have been realized. First, the electric fields at which breakdown of the dielectric occurs are, in general, much larger in polymers ($\gtrsim 10^8$ V/m) than in common liquids ($\approx 10^7$ V/m). Electrochromic effects in polymeric solutions can therefore be made very large by applying high fields; in favorable cases even a saturation regime can be reached. Secondly, at temperatures well below the glass-point of the polymer matrix, T_g, the orientations of the solute molecules are practically fixed. At temperatures around or above T_g, on the other hand, the solute molecules are free to orient themselves in an applied field. Hence, it is possible to obtain samples in which the solute molecules have a frozen-in anisotropic distribution of orientations controlled by the magnitude of an orienting electric field, applied at $T \approx T_g$ and held while cooling down rapidly. It will be clear that the advantages of polymer matrices in comparison with common liquids, outlined above, allow a better experimental discrimination between the several effects contributing to electrochromism.

Dyes suitable for studying electrochromic effects in polymer matrices should have the following characteristics. First, the absorption band of the dye should not overlap extensively with the absorption of the polymer matrix, the glass plates or the electrodes. For our experiments this means that the wavelength of maximum absorbance, λ_{max}, of the dye should exceed 350 nm. Secondly, the molar extinction coefficient of the absorption band of the dye should be rather high in order to allow measurements on rather dilute solutions in which the mutual interaction of dye molecules is minimal. Thirdly, its solubility in the polymer matrix should be sufficient. Finally in order to facilitate the interpretation, the absorption bands should contain single electronic transitions. In the present study the dyes presented in Figure 1 were selected. Though some turned out not to meet all the require-

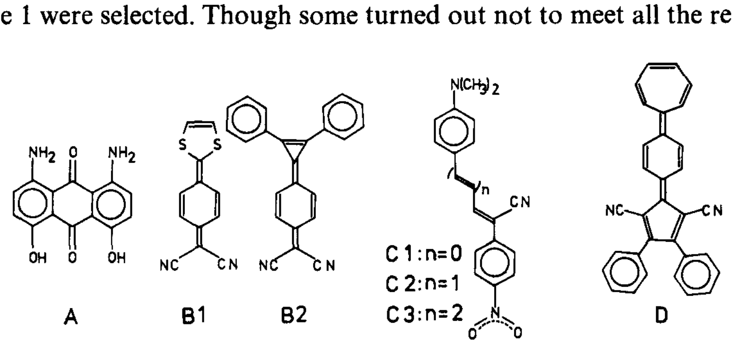


FIGURE 1 Structure formulas of measured dyes.

ments stated above, it will become clear in the discussion that these dyes cover fairly well the range of possibilities to be expected in dipolar organic molecules. Moreover, the compounds C1, C2 and C3 offer the possibility of studying the influence of the length of the π-bonded bridge, connecting donor and acceptor groups of the molecules, on the charge transfer upon excitation. Whereas, theoretically, one expects a rapid decrease of the amount of charge transfer upon a lengthening of σ-bonded bridges, the situation for π-bonded bridges is not clear. The scanty experimental evidence available[2] points to only a very slight decrease with increasing length of π-bonded bridges.

EXPERIMENTAL

1 Synthesis

For the preparation of compounds B1: 7,7-vinylene-8,8-dicyano-*p*-benzochinodimethane and B2: 1-(2,3-diphenyl-cyclopropylidene)-4,4-dicyanomethylene-cyclohexadien-2,5, the method given by Gompper *et al.*[3] was used. Compounds C1: 1-cyano-1-(*p*-nitrophenyl)-2-(*p*′-dimethyl-aminophenyl)-ethene and C2: 1-cyano-1-(*p*-nitrophenyl)-4-(*p*′-dimethyl-aminophenyl)-butadien-1,3 were synthesized in accordance with the procedures, reported in Refs. 4 and 5, respectively. Compound C3: 1-cyano-1-(*p*-nitrophenyl)-6-(*p*′-dimethyl-aminophenyl)-hexatrien-1,3,5 was prepared via a slightly modified method as given in Refs. 4 and5, starting from 4-(*p*-dimethylaminophenyl)-pentadienaldehyde.[6] Compound D: 10,11-diphenyl-9,12-dicyano-(5.6.7)-quinarene was synthesized following the procedure given by Takahashi and Takase.[7]

2 Sample preparation

A solution of both dye and polymer (polymethyl methacrylate (PMMA), Elvacite 2009) in chloroform or acetone is poured onto a teflon plate and the solvent is allowed to evaporate slowly, first at room temperature; then at 120–135°C in vacuo. A few layers of foils obtained in this way are hot-pressed between transparent electrodes (indium oxide on glass plates). The resulting sample (dye concentration 10^{-4} mol/kg, polymer dimensions $20 \times 10 \times 0.1$ mm^3, typically) is placed in a Cary 17 spectrometer, equipped with a sample holder, which allows the application of high DC field strengths over the sample (0–10 kV) and a temperature control between -100°C and $+150$°C by way of a steady flow of (cooled or heated) nitrogen. The unpolarized lightbeam of the spectrometer is perpendicular to the electrodes.

In our samples no dye crystallites were observable neither by microscopic inspection nor by light scattering methods. In general, the molecular constants derived from an analysis of the electrochromism as well as the shape and position of the absorption bands were found to be independent of the dye concentration, indicating that indeed molecular solutions were prepared. However, for dyes B2 and, possibly, B1 the presence of dimers could not be excluded (*vide infra*).

3 Electrochromic measurements

For some 20–40 different wavelengths the influence of DC electric fields on the absorption spectrum at room temperature was measured, both for virgin and for poled samples. The poled samples were obtained by applying a high DC field across the sample at a temperature $T_1 \approx T_g$ ($\approx 110°$C for PMMA) for several minutes, followed by rapid cooling down to room temperature while holding the field. The poling temperature T_1 was chosen such that the field-induced absorbance change occurred within 10–50 seconds; it was verified that at still higher temperatures the field effect did not change, indicating an essentially free reorientation of the solute molecules.

The poling process does not create high internal fields which might be expected to arise from a conceivable charge injection and/or trapping. This is evident from the absence of any shift and/or broadening of the absorption band in the poled sample (compare Eqs. 2 and 3, below).

4 Dielectric measurements

For compounds C1, C2 and C3 the ground state dipole moment was determined from dielectric constants, measured on dilute solutions of the appropriate compound in tetrachloroethene or a mixture of this solvent with *p*-dichlorobenzene (1 : 4), at 25°C and 200 kHz, with the help of a Wayne Kerr bridge B 201. The dielectric constant of dyed polymers was calculated from the capacitance of the hot-pressed samples, measured at 1 kHz and a specified temperature, by means of a General Radio 1656 Impedance Bridge.

THEORY

A theory of electrochromic effects of liquid solutions has been worked out by Liptay[8] and an extension to high-field effects was given by Yamaoka and Charney.[9]

Model calculations, carried out for our compounds, indicated that all effects arising from polarizability terms are only of the order of one percent of the dipolar effects. Therefore only dipolar terms are retained in the evaluation of our electrochromic data. Depending on the experimental conditions, the following electrochromic effects are observed.

1) A change in the field-free measured absorbance of a poled sample ($A(p)$) as compared with that of the virgin sample ($A(v)$), caused by a redistribution of the orientation of dipoles. The magnitude of this effect is given by:

$$\frac{A(p)}{A(v)} = 1 - \tfrac{1}{2}(3\cos^2\psi - 1)\left(1 - \frac{3\coth(x)}{x} + \frac{3}{x^2}\right) \tag{1}$$

where ψ is the angle between the transition matrix element, $\vec{m}$, and the ground state dipole moment, $\vec{\mu}_0$. The parameter x is the ratio between the maximum orientation energy of the dye molecule in the applied field and the thermal energy at the poling temperature $T_1 : x = f\,|\vec{\mu}_0| \cdot |\vec{F}|/kT_1$, where f is a factor converting the external field F into a local field.

2) A field-broadening of the absorbance band, both for poled and for virgin samples:

$$h^2\langle(\Delta\nu)^2\rangle = \tfrac{1}{5}y^2(2 - \cos^2\eta) + \cdots. \tag{2}$$

Here η is the angle between $\vec{m}$ and the difference between the dipole moments in the excited and the ground state of the dye molecule, $\overrightarrow{\Delta\mu} = \vec{\mu}_1 - \vec{\mu}_0$. Furthermore, y is the maximum difference in the shifts of the energy levels in the measuring field; $y = f\,|\overrightarrow{\Delta\mu}| \cdot |\vec{F}|$.

3) In poled samples a field-induced shift of the absorption band occurs:

$$h\langle\Delta\nu\rangle = \tfrac{1}{5}xy(\cos\psi\cos\varphi - 2\cos\eta) + \cdots. \tag{3}$$

Here φ is the angle between $\vec{\mu}_0$ and $\overrightarrow{\Delta\mu}$.

The shift $h\langle\Delta\nu\rangle$ as well as the broadening $h^2\langle(\Delta\nu)^2\rangle$ are determined by fitting some 20–40 points of the measured absorbance curves to the function:

$$\frac{A(\nu, F)}{\nu} = \frac{(1+\delta)A(\nu, 0)}{\nu} + \langle\Delta\nu\rangle\frac{\partial[A(\nu, 0)/\nu]}{\partial\nu} + \tfrac{1}{2}\langle(\Delta\nu)^2\rangle\frac{\partial^2[A(\nu, 0)/\nu]}{\partial\nu^2} \tag{4}$$

Here δ is a constant ($\ll 1$) comprising any residual reorientation terms still present in the glass phase as well as the influence of field-induced changes in the transition moment. The local field was calculated with a generalized Onsager model, ignoring any possible difference in polarizability of the ground state and that of the excited state. Hence, the field factor is (see, for example, Ref. 10):

$$f = \varepsilon(D_1\varepsilon_\infty + 1 - D_1)/[D_1\varepsilon_\infty + (1 - D_1)\varepsilon] \qquad (5)$$

In this model the solute molecule is represented by an ellipsoid, having an optical permittivity, ε_∞, embedded in a matrix with a static permittivity ε. The dipole moment of the molecule is a point-dipole in the centre of the ellipsoid, parallel to one of its main axes, and D_1 is the depolarization factor in that direction. For compounds C1, C2 and C3, ellipsoids with a c/a ratio of 2.1, 2.4 and 2.7, respectively, were chosen on account of molecular models, assuming the conjugate bridge to be all-trans, with the nitrophenyl- and the dimethylaminophenyl-group in the (*E*)-configuration. These c/a ratios lead to D_1-values of 0.165, 0.142 and 0.124, respectively. A spherical model ($D_1 = \frac{1}{3}$) was chosen for the other dyes; for compound A on account of molecular dimensions, for the other compounds as a rough approximation. In the latter case realistic ellipsoids are hard to define and moreover for various reasons (see discussion), the experimental accuracy obtained was rather low.

For molecules with two planes of symmetry, such as A, B1, B2 and D, both $\vec{\mu}_0$ and $\overrightarrow{\Delta\mu}$ are parallel to the line of intersection, while $\vec{m}$ is either parallel or perpendicular to it. In such cases the values of $|\vec{\mu}_0|$ and $|\overrightarrow{\Delta\mu}|$ follow directly from the measured electrochromic effects. If such a symmetry is absent (e.g. compounds C1, C2 and C3), circumstantial evidence may be used to disentangle the intervectorial angles, which is necessary to give a quantitative interpretation of the electrochromic data.

RESULTS

The dipole moments of the dye molecules, as determined from electrochromic measurements on PMMA solutions, are given in Table I. We have listed also the sum of the local dipole moments, $\sum \vec{\mu}_{\mathrm{local}}$, for each compound, calculated from standard group moments.[11] Furthermore ground state dipole moments for C1, C2 and C3 are given as derived from dielectric measurements.

The angles ψ, φ and η in these molecules were derived assuming a planar geometry ($\eta = \psi \pm \varphi$). The values given in Table I should be regarded as estimates of the order of magnitude, rather than as proper measurements of the angles. The values of $\overrightarrow{\Delta\mu}$, calculated with the help of these angles, are 54, 73 and 88.10^{-30} C.m, respectively. The accuracy of the dipole moments given in Table I varies from about 3% for compounds C to about 10% for D; the dielectrically determined dipole moments are accurate within ±2%.

TABLE I

Results of electrochromic measurements of dyes in PMMA

Compound	A[a]	B1	B2	C1	C2	C3	D
λ_{max}[nm] (in PMMA)	635	644[b]	505	445	465	498	700[c]
$\lvert\vec{\mu}_0\rvert$ (diel.) [Cm] * 10^{30}	—	—	—	30.5	34.4	37.3	—
$\lvert\vec{\mu}_0\rvert$ (opt.) [Cm] * 10^{30}	10.0	55	47	28.0[d]	31.6[d]	35.2[d]	106
$\overrightarrow{\Delta\mu}$ (shift) [Cm] * 10^{30}	+8.8	−7	−7	+51.8[e]	+70.5[e]	+84.3[e]	−67
$\lvert\overrightarrow{\Delta\mu}\rvert$ (broad.) [Cm] * 10^{30}	9.3	7	7	57.4[f]	77.2[f]	91.5[f]	83
$\lvert\vec{\mu}_1\rvert$ [Cm] * 10^{30}	19	47	40	84	108	125	33
ψ (degrees)	90	0	0	12	12	12	0
φ (degrees)	0	0	0	6	6	6	0
$\lvert\sum\vec{\mu}_{local}\rvert$ [Cm] * 10^{30}	12	13	13	17	17	17	7

[a] Measured in Epikote 1001 matrix.

[b] The absorption spectrum also contains strong bands at 593 and 554 nm, with a shoulder at ≈525 nm.

[c] Due to the very solvatochromic nature of D and the use of cosolvents, the absorption maximum depends on the sample preparation.

[d] $|\mu_0| \cdot \sqrt{(3\cos^2\psi - 1)/2}$

[e] $\overrightarrow{\Delta\mu}\,(2\cos\eta - \cos\psi\cos\varphi)/\sqrt{(3\cos^2\psi - 1)/2}$

[f] $|\overrightarrow{\Delta\mu}|\sqrt{(2 - \cos^2\eta)}$

DISCUSSION

From a quantumchemical point of view dipole moments in non-centrosymmetric molecules may arise from two different effects. The first, and best-known, effect is the influence of differences in electronegativity (or, in quantumchemical terms, Coulomb integrals) of the various atoms constituting the molecule, and it results in mainly local variations in the charge density. If the excess charge on one atom is approximately cancelled by opposite charges on neighbouring atoms, the molecule is said to possess a local dipole moment (or a number of such moments); otherwise, one has a so-called "Zwitterion." The second effect that may lead to the occurrence of dipole moments in organic molecules is confined to π-electron systems and the stabilization of dipolar structures is, in this case, brought about by exchange integrals. Resonance energy may be gained if the π-electron distribution is such that aromatic rings are present (2, 6, 10, ..., π-electrons per ring: Hückel rule). If in a molecule, starting from an even distribution of electrons over the various atoms, transfer of one electron from one ring to another results in two or more resonating rings, the gain in resonance energy is large enough to overcome the loss in Coulomb energy, and the dipolar structure will be stable. Of course, mixed cases may occur: transfer of electron-density from a ring (with concomitant gain in resonance energy) to an electronegative atom or group of atoms (gain in Coulomb energy).

Local dipole moments are rather small ($< 13.10^{-30}$ C.m.), but may be slightly enhanced by polarizability effects. The dipole moments of "Zwitterions" may be quite large. In both cases the Coulomb integrals—which are the source of the dipole moment in the ground state—are practically unaffected by electronic excitation. Hence, apart from small variations in polarizability effects, the dipole moment will not change upon excitation. Dipole moments originating from a gain in resonance energy may be small (e.g. azulene)[12] as well as large (e.g. calicene);[13] in general a strong back-transfer of charge will occur upon excitation (disappearance of resonance energy in the excited state).

Compound A is an example of a molecule with local dipole moments (the hydroxy- and amino-groups); its electrochromic behaviour being typical for most dipolar organic molecules.

Compounds B1 and B2 are best described as "Zwitterions", originating from the strong electronegativity of both cyano-groups, and probably stabilized further by the resonance energy of the donor ring-systems (see Figure 2). The small values of $|\overrightarrow{\Delta\mu}|$ indicate the predominance of electronegativity effects. At high fields marked deviations from a quadratic field behaviour of the orientation electrochromism were observed for these compounds, in accordance with the large value of $|\vec{\mu}_0|$ derived from low-field electrochromism. However, analysis of this behaviour for B1 led to the conclusion that the four peaks, observed in the absorption spectrum, contained not only contributions from transitions with $\psi = 0°$, but from transitions with $\psi = 90°$ and/or dimers as well. Low temperature spectra (taken at $-100°$C) showed indeed a splitting of all four peaks. Because of this complication, the quantitative aspect of the analysis of the electrochromism of B1 is rather poor. Solutions of B2 in PMMA were slightly contaminated with non-electrochromic dimers, absorbing light in the same spectral

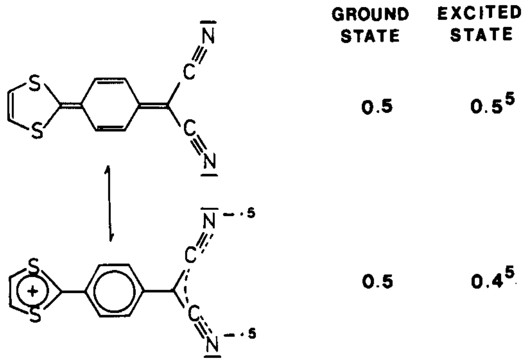
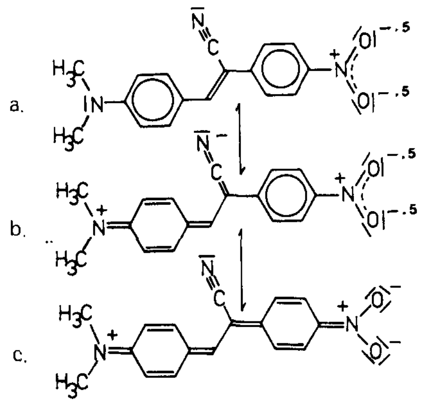


FIGURE 2 Mesomeric structures and relative abundance in ground state and excited state of B1.

region as the monomers. In epoxy resin matrices there are virtually no dimers, enabling a quantitative evaluation to be made of the high-field behaviour of this compound. Preliminary results indicate that, for this compound, the function $G(x) = (1 - 3\coth(x)/x + 3/x^2)$ describes the high-field orientational electrochromism correctly, pointing out that a single transition with $\psi = 0°$ is present.

The ground state dipole moments $|\vec{\mu}_0|$ of the compounds C can be considered, in first instance, as local moments, but comparison with $|\sum \vec{\mu}_{\text{local}}|$ (see Table I) shows an appreciable enhancement. Moreover, the enhancement increases with increasing length of the molecule. One may visualize this in terms of mesomeric structures (see Figure 3). The large observed values of $|\overrightarrow{\Delta\mu}|$ indicate that the dipolar structures (b) and/or (c) (see Figure 3) are much more important in the excited state than in the ground state. If the transfer of half an electron is assumed to occur between the nitrogen atoms of the —CN group and the —$N(CH_3)_2$ group, calculated values of $\Delta\mu$ agree well with the observed values. A similar agreement cannot be obtained for an assumed transfer between the —NO_2 group and the —$N(CH_3)_2$ group. This suggests that the dipolar structure (b) makes a larger contribution to the excited state than structure (c), which is in accordance with the fact that less resonance energy is lost in (b) than in (c). It may be noted that, within the experimental errors, $|\overrightarrow{\Delta\mu}|(\text{Cl}) - |\overrightarrow{\Delta\mu}|(\text{C2})$ equals $|\overrightarrow{\Delta\mu}|(\text{C2}) - |\overrightarrow{\Delta\mu}|(\text{C3})$, suggesting that the amount of charge transferred upon excitation does not decrease significantly upon increasing the distance between donor and acceptor groups.



	GROUND STATE	EXCITED STATE
a.	0.9	0.4
b.	0.0^5	0.5
c.	0.0^5	0.1

FIGURE 3 Mesomeric structures and relative abundance in ground state and excited state of Cl.

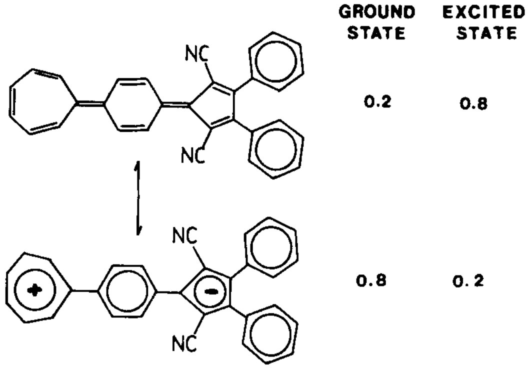


FIGURE 4 Mesomeric structures and relative abundance in ground state and excited state of D.

The stated accuracy for the data of compound D in Table I is rather low (±10%). This is caused by the low solubility of D in polymer matrices. A better solubility is obtained by the addition of cosolvents to the polymer (e.g. chloranil or ethylene-carbonate), at the expense of a poorer reproducibility for measurements on different samples. Nevertheless, without any doubt, the $|\vec{\mu}_0|$ – value of D is remarkably large. Compound D may be regarded as a nice example of an organic molecule in which a large dipole moment in the ground state originates from a gain in resonance energy (see Figure 4). In the excited state the expected, almost complete, back-transfer of

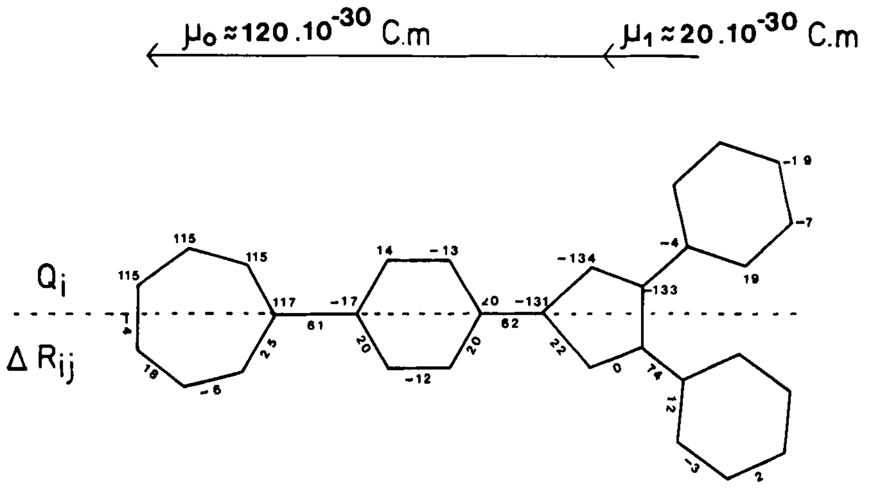


FIGURE 5 Results of SCF-Hückel calculation on 10,11-diphenyl-(5.6.7)-quinarene. Excess charge Q_i in 10^{-3} e, distances R_{ij} (calculated by $R_{ij} = 1.5544 - 0.2436\, P_{ij}$) are given as differences $\Delta R_{ij} = R_{ij} - 1.392$ [Å].

charge is indeed observed. SCF-Hückel calculations, incorporating the Streitwieser ω-technique ($\omega = 1.40$)[14] as well as a relation $\beta_{ij} = 0.68 + 0.48P_{ij}$, to account for the influence of the bondorder P_{ij} on resonance integrals, were carried out for the parent hydrocarbon of compound D. The results (see Figure 5) confirm the explanation of the electrochromic data on *D*, given above: in the ground state all rings are essentially aromatic (almost equal distances R_{ij}) and the calculated charges lead to a large dipole moment (120.10^{-30} C.m., comparable in magnitude to that observed for D), which decreases by an order of magnitude upon excitation.

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