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Survey of the Methods for the Determination of Charge Distribution in Electronically Excited Molecules

By H. Labhart

Ciba Ltd. and University of Basel (Switzerland)*

1. *Introduction*

In sufficiently dilute solutions the lifetimes of molecules in their lowest electronically excited states are largely compared to their vibrational lifetimes. Then they are able to reach equilibrium and behave, with respect to their geometrical, dielectric, optical and chemical properties, as molecules of another sort. Because the energy acquired upon absorption of a quantum of ultraviolet or visible light is comparable to chemical bond energies, one expects and observes[1] considerable deviation from the properties of the molecules in the ground state.

In efforts to predict the chemical activity of molecules with a system of conjugated double bonds, the charge distribution has often been correlated with the velocity constants for electrophilic and nucleophilic substitution at the individual atoms of the system. The empirically found correlation suggests the possibility of explaining the course of photoreactions of conjugated systems on the basis of the charge distribution in the excited state. In addition, knowledge of this molecular property provides insight into the changes in charge distribution occurring upon light absorption. In recent years attempts have been made in several laboratories to determine the charge distribution in excited states by calculation and by experiment.

The chemical theories usually do not deal with the detailed spatial charge density, as determinable from X-ray investigations of molecules in the ground state for example. Instead, the total charge distribution is characterized by a system of charge excesses and deficiencies localized on the atoms. In the following the expression *charge distribution* refers to this system of atomic charges q_i.

While it is possible to calculate the atomic charges q_i in excited states by means of the familiar methods of approximation, it is not yet possible to determine them directly. By observation of the effect of substitution upon the light absorption, however, one can estimate the *changes* in the atomic charges occurring upon excitation. On the other hand, it is possible to measure the change in dipole moment upon optical excitation through the influence of solvents or external electric fields upon the light absorption. The dipole moment of a luminescent molecular state is also accessible through determination of the degree of polarization of the luminescence in an electric field. Although the dipole moments do not yield the atomic charges q_i specifically, they are nevertheless necessary and appropriate quantities for testing the degree of approximation attained by the theory. The methods mentioned differ from and supplement one another in an interesting manner. It seems appropriate therefore to give a survey of the present state of these investigations.

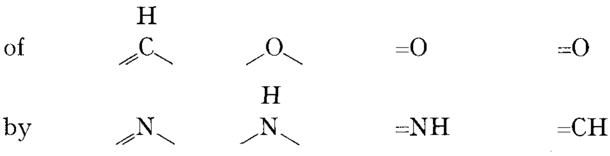
2. *Changes in charge density from substituent effects*

The quantity α_r is to indicate the energy of an electron localized on atom r of a conjugated system. If upon optical excitation the number of electrons on atom r is changed by $\Delta q_r = q_{r1} - q_{r0}$ (q_{r1} and q_{r0} are the charges on atom r in the excited and ground states respectively), then there results a contribution $\alpha_r \cdot \Delta q_r$ to the excitation energy. If the atom r is replaced by another, or affected by a substituent in such a manner that α_r is changed to α_r', then the wave number of the absorption band is changed by

$$\Delta \bar{\nu} = \frac{1}{h\,c}\,(\alpha_r' - \alpha_r)\,\Delta q_r\,.$$

It is assumed here that the chemical change involved is such that (1) Δq_r is not affected significantly and (2) the π-electrons remain distributed over the same atoms, i.e. no mesomeric substituent effects are involved.

Condition (2) is fulfilled in the case of the substitution



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* Present address: Physikalisch-chemisches Institut der Universität Zürich (Switzerland).

[1] J. C. D. Brand and D. G. Williamson, Adv. phys. org. Chem. *1*, 365 (1963), Review.

The change in the α-value of a C-atom upon substitution of H by halogens, –OH etc., on the other hand, is associated with a scarcely negligible extension of the conjugated system. As a result of the possibility of hyperconjugation the fulfilment of condition (2) is also uncertain with substitution of H by CH_3. HEILBRONNER[2,3] has examined this question for azulene in particular and has arrived at the conclusion that the band shifts resulting from changes in α_r outweigh those due to mesomeric effects of the CH_3-group. In certain positions there were, admittedly, deviations from the band shifts calculated with neglect of hyperconjugation, which were accounted for by inclusion of the mesomeric effect.

Methylation is favorable with respect to condition (1) because it insolves a relatively small charge $\Delta\alpha_r$ and thus a small perturbation of the eigenfunctions of the unsubstituted molecule. Aza-substitution of carbon in a conjugated system is a stronger modification as shown by the comparison

$$\frac{1}{h\,c}\,\Delta\,\alpha_{r\,-\,\mathrm{CH_3}} \approx 3400\,\mathrm{cm}^{-1}/\mathrm{Electron}^2$$

and

$$\frac{1}{h\,c}\,\Delta\,\alpha_{r\,-\,\mathrm{Aza}} \approx -\,18000\,\mathrm{cm}^{-1}/\mathrm{Electron}^4.$$

Perturbation-theoretical estimates of the effect of $\Delta\alpha_{r\text{-Aza}}$ on Δq_r yield, for polymethines (cyanines) and polyenes, changes in Δq_r,of the order of one hundredth of the electron charge. Although the perturbation of the eigenfunction of linear systems is thus relatively insignificant, the change in the degree of mixing of different configurations resulting upon the introduction of a hetero-atom can lead to large deviations in the case of degenerate or nearly degenerate states, as are often encountered in cyclic systems. WAGNIÈRE[5], for example, found by means of an SCF-Pariser-Parr-Pople calculation on pyridine an increase of about 0.1 electronic charge on the N-atom in the lowest singlet state relative to the ground state. MASON[6] gives a valuable discussion and experimental data in this connection.

The evaluation of substituent effects has the notable advantage over the remaining methods discussed below, in that it allows the determination not only of the change in dipole moment of the molecule but rather of the changes in the charge on individual atoms of the conjugated system. These changes together with charge distribution in the ground state, as obtained from nuclear magnetic resonance measurements[7–9] or with those obtained from SCF calculations whose reliability can be tested by means of the dipole moments obtained, permit the investigation of the charge distribution in excited states.

The carrying out of these investigations generally requires chemical synthesis, a very few physical aids, but considerable prudence in the interpretation of the results.

3. *Changes in dipole moment from solvent effects*

As seen from a report by LIPTAY[10], the influence of the solvent on the energy states of a dissolved molecule is a phenomenon which is difficult to treat theoretically. However, with the restriction to relatively rough models, the spectral shifts of the optical transitions can be correlated with the dielectric constant of the solvent and with the dipole moments and polarizabilities of the dissolved molecule in the ground and excited states[11,12]. LIPPERT[13] has shown how the changes in dipole moment connected with a transition to the lowest excited singlet state can be derived from the shift of the absorption and fluorescence maxima in various solvents. Lippert's theory is based on the conception that a molecular dipole located in a spherical cavity in the solvent is subject to the Onsager reaction field originating from the polarization of the surroundings. During the process of optical excitation the orientation polarization of the surroundings is unchanged, while the induced (electron) polarization adapts itself continuously. Within the lifetime of the excited state the orientation polarization of the surroundings assumes a value corresponding to the dipole moment in the excited state. Thus the deactivation by means of fluorescence takes place under the influence

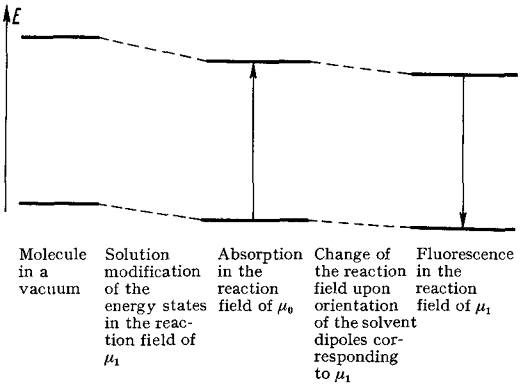

Fig. 1. Effect of the reaction field upon the energy states in absorption and emission under the assumption that μ_1 is greater than and parallel to μ_0.

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[2] E. HEILBRONNER in *Non-Benzenoid Aromatic Hydrocarbons* (Ed., D. GINSBERG; Interscience, 1959), p. 171.

[3] E. HEILBRONNER, Tetrahedron *19*, Suppl. 2, 289 (1963).

[4] J. N. MURRELL, Tetrahedron *19*, Suppl. 2, 277 (1963).

[5] G. WAGNIÈRE, CIBA Basel, not published.

[6] S. F. MASON, in *Physical Methods in Heterocyclic Chemistry* (Ed., A. R. KATRITZKY; Academic Press, 1963), vol. II/1.

[7] G. FRAENKEL, R. E. CARTER, A. MCLACHLAN, and J. H. RICHARDS, J. Am. chem. Soc. *82*, 5846 (1960).

[8] C. MCLEAN and E. L. MACKOR, Mol. Phys. *4*, 241 (1961).

[9] H. SPIESECKE and W. G. SCHNEIDER, Tetrahedron Letters *14*, 468 (1961).

[10] W. LIPTAY, Symposium über Farbenchemie (Elmau 1964), in press.

[11] Y. OOSHIKA, J. phys. Soc. Japan *9*, 594 (1954).

[12] E. G. MCRAE, J. phys. Chem. *61*, 562 (1957).

[13] E. LIPPERT, Z. Elektrochemie *61*, 962 (1957).

of a new reaction field. If the dipole moment of the excited state μ_1 is parallel to and larger than that in the ground state μ_0, then the ground state will be less stabilized than the excited state. Absorption occurs in the weaker reaction field of μ_0, and emission takes place in the stronger reaction field of μ_1 (Figure 1).

As a result the fluorescence spectrum is shifted to longer wave-length by a greater amount than the corresponding absorption band. The formula derived and employed by LIPPERT for the wave number difference of the 0–0 transition in absorption and emission is

$$\Delta \bar{\nu}_{00} = \frac{2\,\Delta f}{h\,c\,a^3}\,(\mu_1 - \mu_0)^2$$

where

$$f = \frac{D-1}{2\,D+1} - \frac{n^2-1}{2\,n^2+1}$$

D = dielectric constant of the solvent, n = refractive index of the solvent, a = radius of the spherical cavity, h = Planck's constant, and c = velocity of light.

The most uncertain quantity in this analysis is surely the cavity radius a. If it is set equal to the radius ϱ of the smallest sphere encompassing the molecule, then the energy of interaction will be underestimated for two reasons. In the first place, the approximation of an extended charge distribution by a point dipole neglects the further stabilization of the higher multipoles in their reaction fields. Secondly, the volume selected will be significantly too large for long extended molecules in particular. LIPPERT finds upon estimating these effects that the choice of $a = 0.8 \cdot \varrho$ should lead to the best value for the difference in dipole moments $(\mu_1 - \mu_2)$.

In view of this uncertainty it would be inappropriate to attempt the perfection of the theory by any of the following refinements: (a) Allowance for the fact that upon absorption the dipole moment of the excited state in the equilibrium configuration of the ground state is involved, while upon emission it is the dipole moment in the equilibrium configuration of the excited state. (b) Consideration of the possibility that the dipole moments of the ground and excited states may not be parallel. (c) Choice of a cavity better fitted to the molecular form, an ellipsoid for example. (d) Consideration of the relatively small contribution due to interaction of higher multipoles with the solvent.

BILOT and KAWSKI[14] found significantly better agreement between the dipole moments obtained from solvent effects and those from other methods (see sections 4 and 5) by including the polarizability in the theory.

However, because the method in this form is applicable only to fluorescent molecules and allows the determination of dipole moments only in the lowest excited singlet states, it is profitable to determine to what extent the shifts in the absorption maxima alone allow conclusions concerning the dipole moments of excited states. If one plots not the difference in wave-length between absorption and fluorescence $\Delta \bar{\nu}_{00} = \bar{\nu}_A - \bar{\nu}_F$, but simply $\bar{\nu}_A$ as a function of Δf, one finds a poor correlation between these quantities. This is understandable in view of the investigations of LIPTAY[10], particularly his equation (105), which indicates that the shift of the absorption maximum depends not only on the difference of the dipole moments of the ground and excited states, but also on the magnitude of the dipole moment in the ground state and the difference in dispersion energies in the ground and excited states. Upon consideration of the corresponding additional terms an approximate evaluation of $(\mu_1 - \mu_0)$ from the shift of the absorption band alone does not seem unpromising.

4. *Changes in dipole moment from band shifts in an electric field*

If an electric field is applied to a system of mobile molecules in the gas phase or in fluid solution, there results on the one hand a partial ordering because of their dipole moments or the anisotropy of the polarizability and on the other hand the shift of the absorption lines known as the Stark effect. The stark effect depends upon the changes in dipole moment and polarizability associated with the optical excitation as well as the orientation of the molecule with respect to the field. In gas phase spectra of small molecules with resolvable rotational structure a shift of the lines and a change in intensity is to be expected[15]. In solutions of larger molecules, which usually possess broad continuous absorption bands, the field causes a measurable deformation of the band contour. In addition the solution becomes dichroic as a result of orientation effects.

That a molecule which changes its dipole moment upon excitation also suffers a shift of its absorption bands in an electric field can readily be seen from Figure 2 for the simplest case, in which the dipole moments in the ground and excited states are parallel.

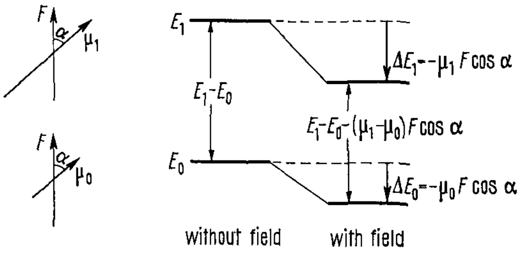

Fig. 2. Relation between line shifts in an electric field and changes in dipole moments upon optical excitation.

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[14] L. BILOT and A. KAWSKI, Z. Naturf. *17a*, 621 (1962).

[15] A. D. BUCKINGHAM, Proc. Roy. Soc. *267*, 271 (1962); Disc. Faraday Soc. No. 35, 48 (1963).

Because the molecules in solution become orientated preferably in such a manner that their dipole moments are parallel to the field, a band shift towards longer wave-length accompanies an increase in dipole moment upon excitation.

The results of various theoretical analyses have recently been compared[16] so that only the formula of LIPTAY and CZEKALLA[17] which is particularly suited for the present discussion will be cited here. For light which passes through the sample in a direction perpendicular to the field F and which is polarized in a direction at an angle χ to the direction of the field there results an extinction coefficient

$$\bar{\varepsilon}_\chi = \frac{\varepsilon_m}{3}\left\{1 + \frac{F^2}{10\,k\,T}\,(2 - 3\sin^2\chi)\left[\sum_{ij} m_i\,m_j\left(\frac{\mu_i\,\mu_j}{k\,T} + \alpha_{ij}\right) - \left(\frac{\mu^2}{3\,k\,T} + \bar{\alpha}\right)\right] + \right.$$
$$+ \frac{F^2}{5\,h\,c}\,\frac{d\ln\varepsilon/\bar{v}}{d\bar{v}}\left[(2 - 3\sin^2\chi)\sum_{ij} m_i\,m_j\left(\frac{\mu_i\,\Delta\,\mu_j}{k\,T} + \frac{\Delta\,\alpha_{ij}}{2}\right) + (1 + \sin^2\chi)\sum_i\left(\frac{\mu_i\,\Delta\mu_i}{k\,T} + \frac{\Delta\,\alpha_{ii}}{2}\right)\right] +$$
$$\left. + \frac{F^2}{10\,h^2\,c^2}\left[\left(\frac{d\ln(\varepsilon/\bar{v})}{d\bar{v}}\right)^2 + \frac{d^2\ln(\varepsilon/\bar{v})}{d\bar{v}^2}\right]\left[(2 - 3\sin^2\chi)\sum_{ij} m_i\,m_j\,\Delta\mu_i\,\Delta\mu_j + (1 + \sin^2\chi)\sum_i \Delta\mu_i^2\right]\right\},$$

where ε_m = extinction coefficient which the system exhibits upon complete parallel orientation of the molecules if the light is polarized in the direction of the transition moment, m_i ($i = x, y, z$) = direction cosine of the transition moment with respect to the molecular coordinate system, μ_i = component of the dipole moment in the ground state, $\Delta\,\mu_i$ = its change upon excitation, α_{ij} = component of the static polarizability tensor in the ground state, $\Delta\,\alpha_{ij}$ = its change upon excitation, and $\bar{\alpha} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$ = average polarizability in the ground state.

The assumption that the intensities of the transitions are unchanged, which was adopted in the derivation of this formula, is probably only decisive in exceptional cases of relatively weak transitions. The perturbation elements of the energy matrix caused by the field are of the order of magnitude of 7–10 cm^{-1}. The intensity borrowing which thus occurs extends chiefly to the neighbouring transitions within 100 cm^{-1}, i.e. less than the band width in solution spectra and comparable to the spectral slit width normally employed in the measurements.

The determination of the change in dipole moment of a band is most facile if the angle χ is chosen equal to 54.7°, for which those terms of the above equation containing the factor $(2 - 3\sin^2\chi)$ vanish. The terms

$$\sum_i\left(\frac{\mu_i\,\Delta\mu_i}{k\,T} + \frac{\Delta\,\alpha_{ii}}{2}\right) \quad \text{and} \quad \sum_i \Delta\mu_i^2,$$

which then remain as unknowns, can be determined individually by measurement of the changes in extinction coefficient caused by the electric field. When the direction of the dipole moment as well as that of its change are determined by the molecular symmetry and the influence of the change in polarizability can be neglected, then both the sign and the magnitude of the change in dipole moment can be given. This is also possible to a good approximation when the molecular structure requires that the change in dipole moment and the dipole moment in the ground state be *almost* parallel or antiparallel. The 4,4'-disubstituted stilbenes may be cited as examples.

Upon neglect of the term $\sum_i \Delta\alpha_{ii}/2$ false results may be obtained for small changes in dipole moment. In such cases $\sum_i \Delta\alpha_{ii}/2$ could be determined from the measurement of the change in extinction coefficient in solid solution (glass) in which the term $\sum_i \mu_i\,\Delta\mu_i/k\,T$, which depends on molecular orientation, disappears and is included as a correction in the analysis. It should be noted that this method yields the difference between the dipole moment of the ground state averaged over the molecular vibrations and that of the corresponding excited Franck-Condon state of the same geometry. However, since the intensities of the IR-transitions indicate that the changes in dipole moment resulting from distortion from the equilibrium position are small compared to the dipole moment itself, the dipole moments of excited states obtained in this manner may be regarded as representative for their equilibrium configuration.

For the local field at the molecule one best adopts the value $F = (D + 2)/3\,F_0$, where D is the dielectric constant of the solvent and F_0 the field in the empty cell. The choice of a polar solvent with higher dielectric constant in order to obtain a larger field at the molecule is inadvisable because the formula given above can then lead to significantly inaccurate values as a result of increased interaction with functional groups of the dissolved molecule and of aggregate formation.

Fields which are sufficiently weak so as to cause no electrical break-down in organic solvents effect changes in the optical density of the order of 0.01%. These effects cannot be measured with conventional spectrophotometers. The necessary methods have been discussed elsewhere[16,18].

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[16] H. LABHART, Tetrahedron *19*, Suppl. 2, 223 (1963).

[17] W. LIPTAY and J. CZEKALLA, Z. Elektrochemie *65*, 721 (1961).

[18] H. LABHART, Chimia *15*, 20 (1961).

5. *Dipole moments of excited states from the polarization of luminescence spectra in an electric field*

The average lifetime of molecules in the lowest singlet or triplet states is sufficiently long to allow, in not too viscous solutions, a molecular distribution corresponding to thermal equilibrium. If an electric field is applied to a luminescent solution, then an ordering occurs corresponding to the dipole moments of the excited molecules, which in turn gives rise to a measurable degree of polarization of the luminescence.

The polarization of fluorescence was first measured by CZEKALLA[19] and was related to the dipole moment of the molecule in the lowest excited singlet state by a simple theory which neglects the Stark effect. If I_p and I_s are the intensities of the fluorescence polarized parallel and perpendicular to the field direction, respectively, then the degree of polarization is given by

$$p = \frac{I_p - I_s}{I_p + I_s} = \frac{1}{20} (3 \cos^2\alpha - 1) \left(\frac{\mu_1}{k\,T}\right)^2 F^2$$

where F = electric field strength at the molecule, μ_1 = dipole moment in the excited state, and α = the angle between μ_1 and the transition moment of the fluorescence band.

Later investigations, carried out with monochromatic irradiation and monochromatic analysis of the fluorescence emission[20], showed that measurements at wave-lengths at which the spectral emission curve is extremely steep must be corrected by as much as 20% because of the shift of the absorption and emission bands in the electric field. LIPTAY[21] has developed a comprehensive theory of this effect which further allows for the circumstance that in certain cases the equilibrium orientation is not attained completely within the lifetime of the excited state. Of course, the general formula contains so many other mostly unknown quantities related to both the ground and excited states that an evaluation of the dipole moment in the excited state is only possible upon the introduction of certain special assumptions about its direction, about the direction of the optical transition moment, and about the magnitude of the polarizability terms. However, such assumptions can be justified in many cases in which the formula then allows the determination firstly of the dipole moment in the fluorescent state from the degree of orientation, and secondly of the change in dipole moment upon the transition to the ground state from the band shift. When the value of the dipole moment in the ground state is allowed for then there is good agreement, as in the cases studied between the dipole moments in the excited states determined by the two methods. Complete agreement is not to be expected since the value of the dipole moment in the ground state but with the equilibrium configuration of the fluorescent state should be employed. The deviations thus caused are at present of the same order of magnitude as the remaining uncertainties.

This method for the determination of dipole moments in the lowest excited singlet states has been applied to a number of molecules. However, it should be equally applicable to the determination of the dipole moments of phosphorescent triplet states. The methods of measurement are discussed in references [16, 19] and [20].

6. *Calculation of charge distribution in excited molecular states*

In calculations on π-electron systems with one-electron methods, such as that of Hückel with parameters which allow relatively good reproduction of the spectra, significantly false charge distributions are obtained. This results from the fact that the repulsion of the electrons accumulated at heteroatoms of higher electronegativity is not accounted for and is exhibited by the fact that the calculated values of the dipole moment are substantially too large. If, on the other hand, the parameters are so fitted that the dipole moments obtained are correct, then the agreement between the calculated and measured spectra is so poor that an assignment of the transitions becomes impossible. Thus many-electron theories, in which the Coulomb repulsion of the π-electrons is included, are absolutely necessary for the calculation of charge distribution in excited molecular states.

The semi-epirical approximations of PARISER-PARR[22] and POPLE[23] are well adapted to the treatment of larger π-electron systems, because the approximations adopted simplify the calculations sufficiently without neglect of any physically important conceptions. The basic functions can be made 'self-consistent' (SCF) for the ground state with the method of ROOTHAAN[24] and NESBET[25] by means of iteration with electronic computers with moderate computer time. In the calculation of eigenfunctions of excited states considerable configuration interaction must be included in most cases.

We have calculated the energy states, transition moments, and charge distributions in a sequence of benzene derivatives[26]. The assignment of the transitions to the observed absorption bands was accomplished on the basis of their wave-length, intensity

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[19] J. CZEKALLA, Z. Elektrochemie *64*, 1221 (1960).

[20] J. CZEKALLA, W. LIPTAY, and K. O. MEYER, Ber. Bunsenges. *67*, 465 (1963).

[21] W. LIPTAY, Z. Naturf. *18a*, 705 (1963).

[22] R. PARISER und R. G. PARR, J. chem. Phys. *21*, 466, 767 (1953).

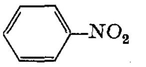
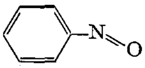
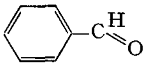
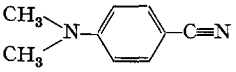
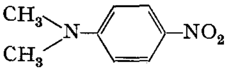
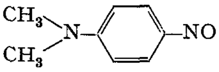
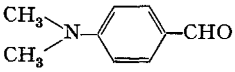
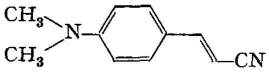
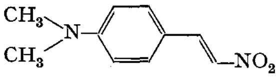
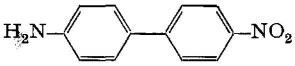
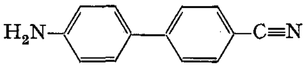
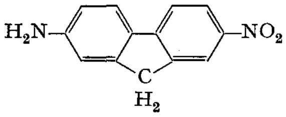
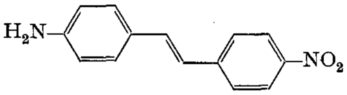
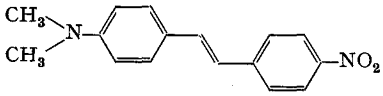
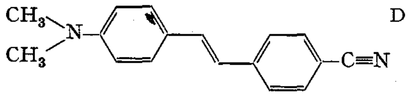
[23] J. A. POPLE, Trans. Faraday Soc. *49*, 1375 (1959).

[24] C. C. J. ROOTHAAN, Rev. mod. Phys. *23*, 69 (1951).

[25] R. K. NESBET, Proc. Roy. Soc. *A 230*, 312 (1955).

[26] H. LABHART and G. WAGNIÈRE, Helv. chim. Acta *46*, 1314 (1963).

Dipole moments of excited molecular states in debyes. Solvents: H = hexane, B = benzene, D = dioxane.
States: G = ground state, S_i = *i*th excited singlet state

Molecule	Solvent	State	Methods of determination					
			Dielectric measurements	Solvent shift		Effect of an electric field upon absorption	Effect of an electric field upon fluorescence	Calculated π-dipole moment
				Evaluation by Lippert[13]	Evaluation by Bilot and Kawski[14]			
	H	G	4,2					5,5
		S_1						
		S_2				9 ± 2[26]		16,3
		S_3						16,5[26]
	H	G	3,14					2,42
		S_1[a]				12,2[26]		12,8
		S_2						9,45
		S_3						2,23[26]
	H	G	2,75					2,78
		S_1						
		S_2				7,1		7,9
		S_3				6,3[26]		6,45[26]
	D	G	6,6					
		S_1		23		12,5[31]	11,1–14,9[20]	
	H	G	6,85					8,8
		S_1				–		16,6
		S_2				14,3[26]		26,7
		S_3				11,8[26]		17,4[26]
	H	G	6,45					5,96
		S_1[a]				13,5		17,7
		S_2				–		12,9
		S_3				13,4[26]		14,8[26]
	H	G	5,6					4,58
		S_1				–		10,7
		S_2				13,3[26]		17,2
		S_3				–		10,9[26]
	H	G	6,95					
		S_1		14[32]		14[31]		
	B	G	7,7					
		S_1		18		18[31]	17,9	
	B	G	6,0					
		S_1		18	15,5	23[31]	22,4[20]	
	B	G	6,0					
		S_1				16,5[31]	15,3–13,0[20]	
	B	G	5,8					
		S_1		25	23,5	23[31]	19,2–18,6[20]	
	B	G	6,5					
		S_1				22[31]	23,4[20]	
	B	G	7,1					
		S		32	25	26,5[31]	25,1[20]	
	D	G	7,1					
		S_1		29		20[31]	21,2–20,2[20]	

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[a] The long-wavelength n–π* transition has not been included.

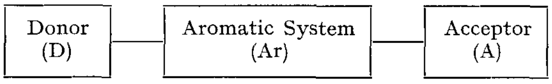
and polarization, and the theoretical π-dipole moments could be compared with the dipole moments obtained by measurement of the effect of an electric field. The extent of agreement is discussed in section 7.

MILLER, LYKOS, and SCHMEISING[27] calculated charge distributions in excited states of some N-heterocyclic molecules by the 'open shell' SCF method. Unfortunately particulars concerning the spectra and a comparison with the measured dipole moments are lacking.

A further many-electron method, the 'molecules in molecules' process[28, 29], can be employed for the calculation of charge distribution in excited states. Calculations of this sort have been performed by GRINTER and HEILBRONNER[30] on *ortho-*, *meta-*, and *para*-disubstituted benzene derivatives and by MURRELL[4] on aniline. The description of molecular states as a combination of locally excited states in individual molecules and of intramolecular charge transfer states thus employed characterizes the molecular states in a very pictorial manner.

7. *Results and discussion*

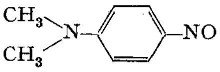
The results of measurements and calculations of dipole moments are summarized in the following Table. Those molecules have been chosen, as a rule, which have been studied by various methods. In all of these compounds of the type



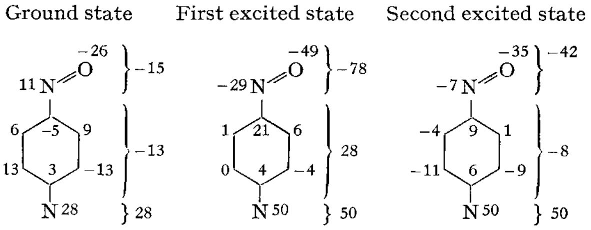
the dipole moments of excited states are larger than those of the ground state, which is generally interpreted on the basis that the mesomeric limiting from $D^+ = Ar = A^-$ plays a larger role in the excited state than in the ground state. LIPPERT[13] and CZEKALLA[31] have pointed out that the dipole moments would have to be much larger than those observed if this limiting form were to play the *major role* in the description of the excited state. It is thus to be expected that intramolecular charge transfer states of the type D^+–Ar^-–A and D–Ar^+–A^- contribute to the excited state in addition to the limiting form D–Ar–A, which is important in the ground state. The degree of participation of such structures, which can scarcely be judged without calculations, was obtained theoretically by GRINTER and HEILBRONNER[30] (see section 6). The results obtained for *para*-disubstituted benzenes are summarized in Figure 3.

The charge distributions XIV and XV in Figure 3 indicate that, upon excitation, the charge passes chiefly from the aromatic ring to the acceptor and that the structure D^+–Ar–A^- does not contribute to this state.

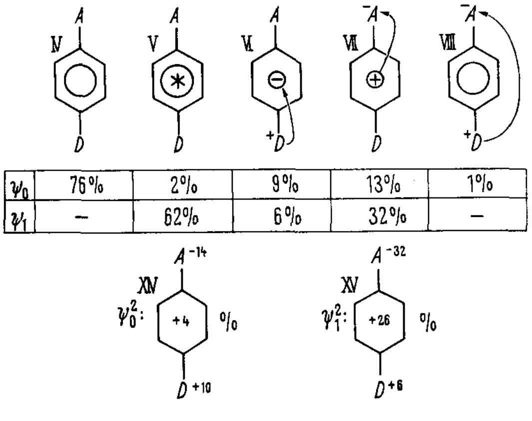
The parameters upon which the calculations of Figure 3 are based correspond approximately to the situation in the molecule



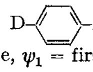
and it is therefore interesting to compare them with corresponding results obtained for this molecule by the SCF–PARISER-PARR–POPLE method[26]. The charge distribution obtained there (in units of $1.6 \cdot 10^{-21}$ Clb) is as follows:



It is seen that a significant shift of charge of the type D^+–Ar–A^- is found in these calculations which influences strongly the change in dipole moment upon excitation. The experimentally determined change in dipole moment of 7 D with respect to the ground state is definitely smaller than the calculated change in the π-moment (11.7 D). On the other hand, one estimates from the charge distribution given by GRINTER and



ψ_0	76%	2%	9%	13%	1%
ψ_1	–	62%	6%	32%	–

Fig. 3. Relative contribution of various limiting structures to the ground and first excited states of DA. From GRINTER and HEILBRONNER[30]. ψ_0 = ground state, ψ_1 = first excited singlet state.

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HEILBRONNER a theoretical change in π-moment of only 2 D, which is too small by about the same amount. However, in both theories the deviations from the experimental values probably depend more on the choice of parameters than on the methods of calculation[33].

Zusammenfassung. Zur Bestimmung der Ladungsverteilungen oder Dipolmomente in elektronisch angeregten Molekülzuständen können die folgenden Effekte herangezogen werden: 1. Einfluss von Substituenten auf die Lage der Absorptions-Maxima. 2. Einfluss von Lösungsmitteln auf die Wellenzahldifferenz der Absorptions- und Lumineszenzbanden. 3. Einfluss eines von aussen angelegten elektrischen Feldes auf die Absorptionsspektren. 4. Einfluss eines äusseren elektrischen Feldes auf den Polarisationsgrad der Fluoreszenz.

Die verschiedenen Modellvorstellungen, welche für die Auswertung solcher Messungen herangezogen werden, sowie theoretische Näherungen zur Berechnung der Ladungsverteilung werden zusammengestellt. Im letzten Abschnitt werden theoretische und experimentelle Resultate für einige Moleküle verglichen und diskutiert.

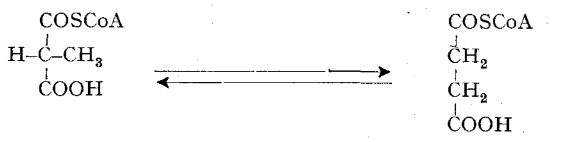
[33] We are indebted very much to Dr. B. SOMERS for translating this report from the German.

SPECIALIA

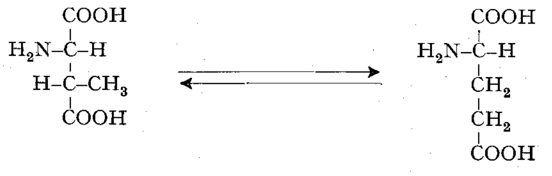
Les auteurs sont seuls responsables des opinions exprimées dans ces brèves communications. – Für die Kurzmitteilungen ist ausschliesslich der Autor verantwortlich. – Per le brevi comunicazioni è responsabile solo l'autore. – The editors do not hold themselves responsible for the opinions expressed in the authors' brief reports. – Ответственность за короткие сообщения несёт исключительно автор. – El responsable de los informes reducidos, está el autor.

Zur Stereochemie der Propandioldehydrase-Reaktion

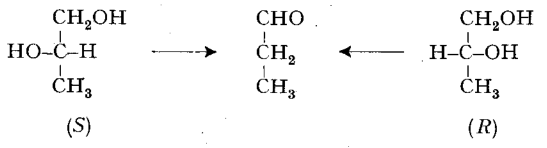
Die drei bestbekannten enzymatischen Prozesse, welche ein B_{12}-Coenzym benötigen, sind die reversiblen Umlagerungen des (*R*)-Methylmalonyl-CoA zu Succinyl-CoA (Gl. 1)[1] und der (2*S*, 3*S*)-Methylasparaginsäure zu (*S*)-Glutaminsäure (Gl. 2)[2], sowie die Dehydratisierung von (*S*)- und (*R*)-Propandiol zu Propionaldehyd (Gl. 3)[3]. Gemeinsames Merkmal der erwähnten Prozesse ist die 1,2-Wanderung eines Wasserstoffatoms. Laut SPRECHER, CLARK und SPRINSON[4] vollzieht sich diese Wanderung unter Retention der Konfiguration im Falle des (*R*)-Methylmalonyl-CoA, nicht aber im Falle der (2*S*, 3*S*)-Methylasparaginsäure, bei welcher Inversion beobachtet wurde[5]. Für die dritte Reaktion hat die Arbeitsgruppe von ABELES kürzlich bewiesen, dass je nach der (*S*)- oder (*R*)-Chiralität des Propandiols spezifisch das eine oder das andere der sterisch nichtäquivalenten Wasserstoffatome des C-1 nach C-2 wandert[6]. Die Frage nach der absoluten Stereochemie des jeweils wandernden Atoms wurde offengelassen. Wir berichten nachfolgend über eigene Resultate, die das stereochemische Bild der Propandioldehydrase-Reaktion vervollständigen.



$$\begin{array}{c}\mathrm{COSCoA}\\ |\\ \mathrm{H{-}C{-}CH_3}\\ |\\ \mathrm{COOH}\end{array} \rightleftarrows \begin{array}{c}\mathrm{COSCoA}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{COOH}\end{array} \qquad (1)$$



$$\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{H_2N{-}C{-}H}\\ |\\ \mathrm{H{-}C{-}CH_3}\\ |\\ \mathrm{COOH}\end{array} \rightleftarrows \begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{H_2N{-}C{-}H}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{COOH}\end{array} \qquad (2)$$



$$\underset{(S)}{\begin{array}{c}\mathrm{CH_2OH}\\ |\\ \mathrm{HO{-}C{-}H}\\ |\\ \mathrm{CH_3}\end{array}} \longrightarrow \begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_3}\end{array} \longleftarrow \underset{(R)}{\begin{array}{c}\mathrm{CH_2OH}\\ |\\ \mathrm{H{-}C{-}OH}\\ |\\ \mathrm{CH_3}\end{array}} \qquad (3)$$

Umsetzung von Brenztraubensäure, **1**, mit Milchsäuredehydrogenase und NAD-^{2}H gab (+)-(*S*)-2-^{2}H-Milchsäure, **2**, deren Methylester mit $LiAlH_4$ zu (+)-(*S*)-2-^{2}H-Propandiol-(1,2), **3**, reduziert wurde. Anderseits lieferte die Reduktion des Methylesters **4** von (−)-(*R*)-Milchsäure mit $LiAl^{2}H_4$ (−)-(*R*)-1-$^{2}H_2$-Propandiol-(1,2), **5**. Durch Inkubation von **3** mit einem zellfreien Extrakt aus *Aerobacter aerogenes* (ATCC 8724) in Gegenwart von Dimethylbenzimidazol-B_{12}-Coenzym[3] entstand ein Propionaldehyd **6**, welches in situ mittels Hefe-Alkoholdehydrogenase und NADH zum Propanol **7** reduziert wurde. Platinkatalysierte Oxydation des letzteren mit Sauerstoff in wässriger Lösung führte zu einer in Stellung

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