  Bull. Chem. Soc. Jpn., 60, 4245—4250 (1987)

Spectroscopic Investigations on 9-(4-Dimethylaminophenyl)-10-cyanoanthracene

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(Received June 4, 1987)

Excited state dipole moments of 9-(4-dimethylaminophenyl)-10-cyanoanthracene determined from the electric field effect on solutions in several solvents as well as fluorescence spectra, ground state absorption and S_n-S_1 transient absorption spectra show that this molecule most probably fluoresces from two excited states in nonpolar and medium polar solvents, whereas only one highly polar excited state emits in polar solvents.

The spectroscopic and kinetic behaviour of 4-(9-anthryl)-*N*,*N*-dimethylaniline (ADMA) and some derivatives has been investigated in several papers.[1-15] In particular, the fluorescence at least in sufficiently polar solvents originates from a polar state which is stabilized in polar solvents through solvent-solute interaction and/or formation of a twisted conformer so that its energy, originally higher than the less polar first Frank-Condon (FC) excited singlet state, becomes the energetically lowest. From electro-optical absorption and emission measurements[7,12] it has been shown that polarizability effects due to mere solvent solute interaction can describe the observed effects, but also a description of the experimental material assuming mere twisting to a so-called "twisted intramolecular charge-transfer (TICT) state" was shown to be possible.[9,12] A crucial point is the interpretation of the electro-optical absorption measurement in the long wavelength shoulder. Here, Herzberg-Teller coupling between two nearby electronic states as discussed with the related compound *p*-dimethylaminobenzonitril (DMABN) and some of its derivatives[16] could cause problems in the interpretation of the measured quantities. Hence, the molecule 9-(4-dimethylaminophenyl)-10-cyanoanthracene (10-CN-ADMA) was synthesized[17] in order to study the effect of a larger charge transfer present already in the ground state on the solvent dependence of the fluorescence. Also there was some hope that the long wavelength shoulder in the absorption spectrum would be broader at least in polar solvents than this is the case with ADMA. Then, electro-optical absorption measurements could be performed with less inherent systematic error than with ADMA.[7]

Experimental

Outline of Electro Optical Absorption (EOAM) and Integral Electro Optical Emission (IEOEM) Measurements. With EOAM, the effect of an external electric field E_a on the absorption $A^E(\tilde{\nu}, \chi)$ of solute molecules is measured dependent on the wavenumber $\tilde{\nu}$ and the angle χ between the direction of E_a and the polarization direction of the linearly polarized light used to measure $A^E(\tilde{\nu}, \chi)$. The method has been worked out extensively by Liptay and co-workers.[18] From a suitable experiment,[19] the experimental quantity $L(\tilde{\nu}, \chi)$ is determined as defined by the following Eq. 1,

$$A^E(\tilde{\nu}, \chi) = A(\tilde{\nu}, \chi)[1 + L(\tilde{\nu}, \chi) E_a^2] \quad (1)$$

From the measured wavenumber and angular dependence of $L(\tilde{\nu}, \chi)$ the terms ${}^aE$ to ${}^aI$ can be determined as shown in Ref. 18. With the transitions considered in this paper, they are related to the molecular dipole moments through the following Eqs. 2 to 4, if only explicit dipole terms have to be taken into account

$${}^aE = 2\beta^2 f_e^2 \mu_g^2 \quad (2)$$

$${}^aF = {}^aG = \beta f_e^2 \mu_g \Delta^a\mu \quad (3)$$

$${}^aH = {}^aI = f_e^2 (\Delta^a\mu)^2 \quad (4)$$

For further definitions see below. Integral electro optical emission measurement (IEOEM)[12,20] are a modified (an integral) version of spectrally resolved electro optical emission measurements (EOEM).[21] With IEOEM the effect of E_a on the fluorescence photon flux $p_1^E(\phi)$ from the whole fluorescence band is measured without spectral resolution in an optical broad band experiment, dependent on the angle ϕ between the direction of E_a and the polarization direction given by an analyzing polarizer in the fluorescence light beam. The method has been described and checked with various systems in refs.[20-23] Equation 5 defines the experimental quantity $\chi_1(\phi)$

$$p_1^E(\phi) = p_1[1 + \chi_1(\phi) E_a^2] \quad (5)$$

From the angular dependence of χ_1, two experimental terms ${}^iD$ and ${}^iE$ can be derived. As is shown elsewhere,[20,22] a linear combination of these quantities is related to the dipole moment of the fluorescent state

$${}^cE = {}^iE - 4{}^iD = 2\beta^2 f_e^2 \mu_e^2 \quad (6)$$

$$\beta = (kT)^{-1} \quad (7)$$

with Boltzmann's constant k and the temperature T.

$$\Delta^a\mu = (1 - f'\alpha_e^{oFC})^{-1} (1 - f\alpha_e^{oFC}) (1 - f\alpha_g^{o})^{-1} (1 - f'\alpha_g^{o}) (\mu_e^{FC} - \mu_g) \quad (8)$$

$$\mu_g = (1 - f\alpha_g^{o})^{-1} \mu_g^{o} \quad (9)$$

$$\mu_e^{FC} = (1 - f\alpha_e^{oFC})^{-1} \mu_e^{oFC} \quad (10)$$

$$\mu_e = (1 - f\alpha_e^{o})^{-1} \mu_e^{o} \quad (11)$$

$$\mu_g^{FC} = (1 - f\alpha_g^{oFC})^{-1} \mu_g^{oFC} \quad (12)$$

μ^o are the dipole moments of the considered equilibrium and Frank-Condon (FC) states of the free solute and α^o their polarizabilities. Subscripts e and g indicate excited state and ground state properties, respectively.

$$f_e = 3\varepsilon/(2\varepsilon + 1) \cdot 1 \quad (13)$$

$$f = [(\varepsilon - 1)/(2\varepsilon + 1)]/(2\pi\varepsilon_o a^3) \cdot 1 \quad (14)$$

$$f' = [(n^2 - 1)/(2n^2 + 1)]/(2\pi\varepsilon_o a^3) \cdot 1 \quad (15)$$

In the used model,[18,21] the solute dipole is approximated by a point dipole in the center of a sphere with radius a, determined by the solute's size. f_e then connects the field in the empty sphere to the externally applied field E_a and f and f' describe the effect of the reaction field due to polarization of the solvent shell around the solute dipole ε_0 is the permittivity of the vacuum. Equation 8 reduces to

$$\Delta^a\mu = \mu_e^{FC} - \mu_g \qquad (16)$$

in nonpolar solvents are used.

Conventional Absorption and Fluorescence Spectra. Ground-state absorption spectra have been measured using a Perkin Elmer-Hitachi model 340 spectral photometer with data handler, connected to a Digital Equipment LSI 13/2 computer with Watanabe WX4671 plotter. Spectral bandwidth was 0.4 nm. The quanta-corrected fluorescence spectra have been recorded using a Farrand MK II fluorometer connected to the mentioned computer system. Quanta calibration of the emission channel was performed using an EG&G 1000 Watts quartz-halogen lamp, calibrated to an NBS-standard. Spectral bandwidth was 2 nm, excitation wavelength was 400 nm.

Transient Absorption Spectra. Picosecond time-resolved transient absorption spectra were measured by means of a microcomputer-controlled, mode-locked Nd^{3+}: YAG laser photolysis system described elsewhere.[24] The third harmonic of a single picosecond pulse was used for excitation.

Compounds. 10-CN-ADMA has been prepared and carefully purified as described else where.[17] All solvents have been purified using standard procedures[25] and were dried under reflux conditions over Na-K-alloy or where this was impossible by chromatography over alumina, immediately before preparing the solutions, undre Ar protective overpressure.

Results and Discussion

Results from EOAM. The long wavelength shoulder of the absorption spectrum of 10-CN-ADMA[17] in dioxane is represented in Fig. 1 and is compared with 9-cyanoanthracene. EOAM investigations have been performed at 298 K in cyclohexane and dioxane solutions. The results are given in Table 1 together with the calculated dipole moments.

The effective ground state dipole moment μ_g does not show a solvent dependence that could be due to a

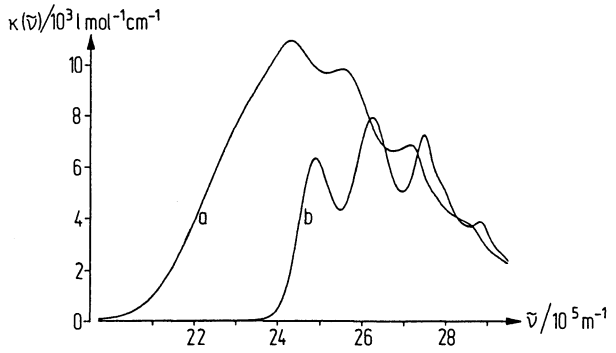

Fig. 1. Absorption coefficient $\kappa(\tilde{\nu})$ within the first absorption band of 10-CN-ADMA (a), compared to that of 9-cyanoanthracene (b), in dioxane at 298 K.

Table 1. Results from EOAM on 10-CN-ADMA

	Cyclohexane	Dioxane
Range	438—455 nm	439—470 nm
${}^aD/10^{-20}V^{-2}m^2$	−420	−720
${}^aE/10^{-20}V^{-2}m^2$	8100±1000	7500±1400
${}^aF={}^aG/10^{-40}CV^{-1}m^2$	3600± 400	5100±400
f_e	1.202	1.223
$\mu_g/10^{-30}Cm$	21.8±1.3	20.6± 1.8
$\Delta^a\mu/10^{-30}Cm$	56.5±10	83.3±15
$\mu_e^{FC}/10^{-30}Cm$	78.3±10	103.9±15

Table 2. Results from IEOEM on 10-CN-ADMA at 298 K in Various Solvents Errors Amount to about 10%

	${}^iD/10^{-20}V^{-2}m^2$	${}^iE/10^{-20}V^{-2}m^2$
Heptane	174	38300
Cyclohexane	0	41700
Dipentyl ether	2200	76800
Dibutyl ether	2340	87100
Dipropyl ether	2200	98800
Diisopropyl ether	2560	113500
Dioxane	186	110200
Fluorobenzene	−1940	111700
Benzotrifluoride	−3910	117400

reaction field induced part and what could be separated using Eq. 9. Hence, $\mu_g=(21\pm2)10^{-30}$ C m is used as an upper limit for μ_g°. This value agrees well with the sum of μ_g° of *N,N*-dimethylaniline and of 9-cyanoanthracene[26] which amounts to $19.1\cdot10^{-30}$ C m.

The change of the effective dipole moment with excitation is found to be solvent dependent, even if the very large experimental error of $\Delta^a\mu$ is taken into account. This is due to the fact that the measurement is done in a slope which is a small part only of the whole absorption to the polar FC-state. Nevertheless, the effective dipole moment μ_e^{FC} is found to be very large in both solvents, although the value of μ_e^{FC} found in dioxane must be discussed as an approximation, since Eq. 16 is not valid in dioxane where reaction field induced terms cannot be neglected. Referring to Eq. 10, obviously μ_e^{FC} in cyclohexane is an upper limit for μ_e^{oFC}.

The values found for $\Delta^a\mu$ are larger than those reported in Table 5 of Ref. 7, which would be in agreement with the model of an intramolecular charge-transfer excited state where the charge centers would be further apart in 10-CN-ADMA than in ADMA itself.

Results from IEOEM. Table 2 represents the experimental quantities ${}^iD$ and ${}^iE$.

Discussion Assuming One Emitting Species or State. If one emitting species or state is assumed, μ_e can be calculated using Eq. 6. The values are given in Table 3. They show a strong solvent dependence which might be interpreted as reaction field induced amounts to the total effective dipole moment μ_e. Then with Eq. 17 from a regression analysis of μ_e^{-1} on $(\varepsilon-1)/(2\varepsilon+1)$, μ_e° as well as the polarizability density

Table 3. Some Results from IEOEM on 10-CN-ADMA Assuming a One State System. Errors of μ_e Are about 5%, Those of μ_e^0 and α_e^0/a^3 Are Derived from the Standard Error of the Regression Coefficients

	$\mu_e/10^{-30}$C m
Heptane	47.4
Cyclohexane	49.4
Dipentyl ether	59.7
Dibutyl ether	62.9
Dipropyl ether	66.9
Diisopropyl ether	70.4
Dioxane	78.7
Fluorobenzene	73.3
Benzotrifluoride	74.7
$\mu_e^0/10^{-30}$C m	37.1±1.8
$(\alpha_e^0/a^3)/10^{-10}$C V^{-1}m^{-1}	0.74±0.13

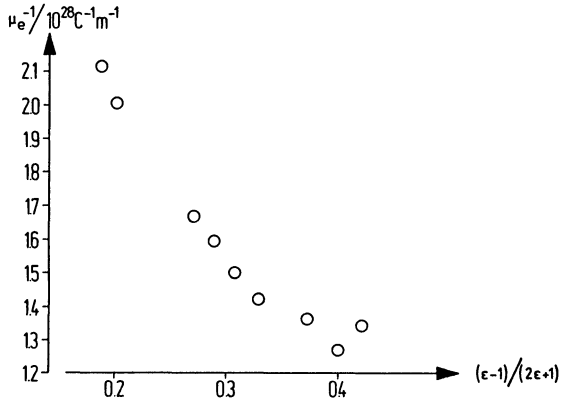

Fig. 2. Plot of μ_e^{-1} of 10-CN-ADMA versus $(\varepsilon-1)/(2\varepsilon+1)$.

α_e^0/a^3 can be derived.

$$\mu_e^{-1}=(\mu_e^0)^{-1}-(\alpha_e^0/(\mu_e^0 2\pi\varepsilon_0 a^3))(\varepsilon-1)/(2\varepsilon+1) \quad (17)$$

Fig. 2 shows a plot according to Eq. 17, which hardly could be interpreted as a straight line. A better interpretation seems to be a curve that levels off to a horizontal line at μ_e around $80\cdot10^{-30}$ C m, at high solvent polarity. Table 3 displays the results from a respective linear regression analysis, too. The permanent dipole moment μ_e^0 seems to be pretty small. Contrasting this, the polarizability density α_e^0/a^3 is pretty large, in the order of what had been reported in Ref. 7 with ADMA. This unusual finding is based on the assumption that only one state or species emits. On the other hand, from investigations on ADMA and some other derivatives[6] as well as from the bent curve of Fig. 2 and from the disagreement between μ_e determined in cyclohexane and μ_e^{FC}, it might follow that perhaps two emitting species or states determine the spectroscopic behavior of 10-CN-ADMA. This idea is also supported by the change of the spectral shape of the fluorescence of 10-CN-ADMA, when going from nonpolar to polar solvents, as shown in Fig. 3.

Discussion Assuming Two Emitting Species or States. For the considerations in this section, terms like $f\alpha_e^0$ are assumed to be much smaller than 1, in all

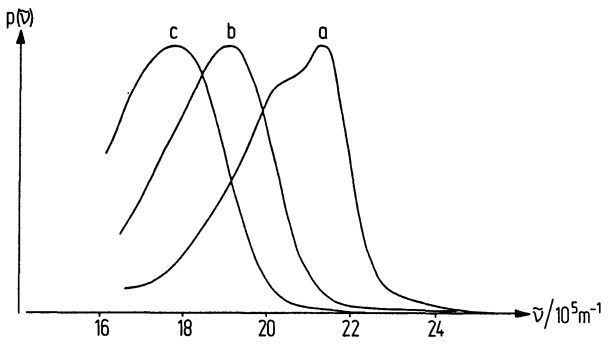

Fig. 3. Fluorescence spectrum of 10-CN-ADMA, a: in methylcyclopentane; b: in diisopropyl ether; c: in fluorobenzene, at 298 K, Excitation wavelength was 400 nm, sample concentration $1\cdot10^{-5}$ mol dm^{-3}.

solvents, that is induced amounts to μ_e are assumed to be negligible, and hence $\mu_e=\mu_e^0$, with the two-state model. Also it is assumed as the working hypothesis in this section, that there are a polar fluorescent species or state A and a less polar fluorescent species or state B which emit simultaneously to give the observed broad fluorescence band. State A may be the intramolecular charge transfer state just discussed and state B probably a locally excited 9-cyanoanthracene like state with some admixture of the dimethylaniline→cyanoanthracene charge transfer character. No assumption is made with respect to the conformation of 10-CN-ADMA in these two states, as to whether the two states are to be considered as conformers. With this model, the solvent dependence of the dipole moment μ_e shown in Table 3 and in Fig. 3 is due to a change of the ratio q of the fluorecence intensities of B and A

$$q=p_{1B}/p_{1A} \quad (18)$$

Consequently, the value of μ_e in polar solvents that gets constant around $\mu_e^0=80\cdot10^{-30}$ C m would be due to almost only the A state emission and $\mu_e^0=47.4\cdot10^{-30}$ C m in heptane might be assumed as due to almost pure B-state emission. Then q can be calculated according to Eq. 19, which is taken from[20]

$${}^cE_A={}^cE_M(1+q)-{}^cE_B q. \quad (19)$$

The values of q are given in Table 4. They are founded on the assumed values for $\mu_e^0(A)=80\cdot10^{-30}$ C m and $\mu_e^0(B)=47\cdot10^{-30}$ C m or alternatively $\mu_e^0(B)=35\cdot10^{-30}$ C m, by which ${}^cE_A$ and ${}^cE_B$ have been calculated according to Eq. 6. In principle, q can be used for the kinetic interpretation of the activation barrier between the two states. A quantitative discussion will be given together with respective data of other related molecules in a forthcoming communication.[27]

S_n-S_1 Absorption Spectra. S_n-S_1 absorption spectra have been measured at 298K in cyclohexame, fluorobenzene, tetrahydrofuran, 1-butanol, and acetonitrile. The measurements suffered from the very low solubility of 10-CN-ADMA in all solvents-which is the reason for the noisy spectra. Figure 4 shows these spectra at

Table 4. The Ratio q as Determined from IEOEM on a Two State Model Basis, Founding on $\mu_e^0(A)=80\cdot10^{-30}$C m and $\mu_e^0(B)=47\cdot10^{-30}$C m*, and $\mu_e^0(B)=35\cdot10^{-30}$C m**

	q*	q**
Heptane	110	4.06
Cyclohexane	17.1	3.26
Dipentyl ether	2.09	1.21
Dibutyl ether	1.40	0.89
Dipropyl ether	0.85	0.59
Diisopropyl ether	0.53	0.39
Dioxane	0.05	0.04
Fluorobenzene	0.32	0.25
Benzotrifluoride	0.24	0.19

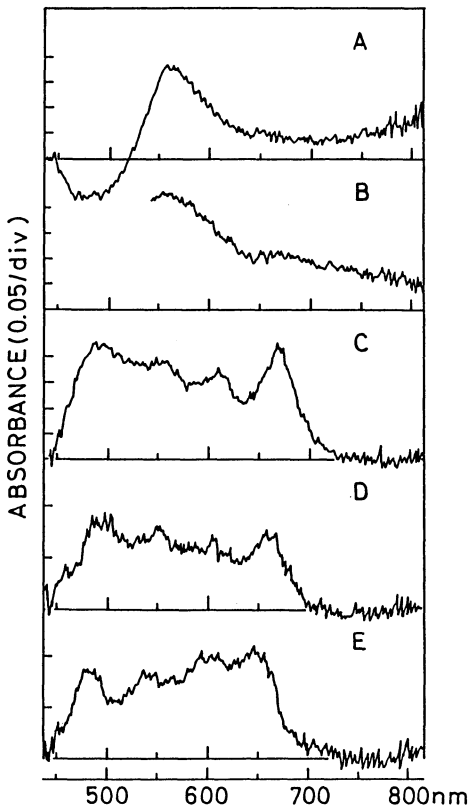

Fig. 4. S_n–S_1 transient absorption spectra of 10-CN-ADMA in some solvents, taken at 298 K, A: in cyclohexane, 100 ps after the 355 nm excitation pulse; B: in fluorobenzene, after 100 ps; C: in tetrahydrofuran, after 200 ps; D: in 1-butanol, after 200 ps; E: in acetonitrile, after 100 ps.

100 ps delay time after the excitation with the laser pulse of about 25 ps duration. The spectral band shape has not indicated any change depending on the delay time except in 1-butanol. Even in 1-butanol the spectral shape has reached its steady state within this time interval. The spectra change considerably when passing from nonpolar to polar solutions. In cyclohexane, an absorption band with peak around 570 nm and broad absorption without distinct peak in 600—800 nm region are observed. This transient absorption spectrum is somewhat similar to that of 9-cyanoanthracene (9-CA) (Fig. 5) as well as that of ADMA

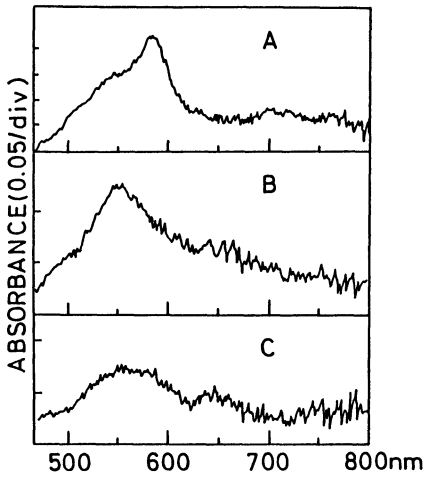

Fig. 5. S_n–S_1 transient absorption spectra, taken at 298 K, of A: 9-CA in cyclohexane, 100 ps after the 355 nm excitation pulse; B: 9-CA+DMA(ca. 0.1 M) in acetonitrile, after 66 ps; C: 9-CA+DMA(ca. 0.1 M) in acetonitrile, after 300 ps.

in cyclohexane solutions.

In tetrahydrofuran, 1-butanol and acetonitrile (Fig. 4), the spectra are very similar to each other, but quite different from that in cyclohexane. The spectral shape in these polar solvents with peaks at 550, 610, and 660 nm is very similar to those of some derivatives of and compounds related to ADMA,[28] where the anthryl moiety is quite isolated from the other part of these compounds, except that the spectra of 10-CN—ADMA are ca. 70—80 nm bule-shifted compared with those of ADMA. It had been emphasized there that the S_n–S_1 spectra of the latter compounds in polar solvents resemble the anthracene anion.[28] In Fig. 5, the transient absorption spectra of 9-CA in cyclohexane (A, at 100 ps delay time) and 9-CA+*N*,*N*-dimethylaniline (DMA) in acetonitrile (B and C, at 66 and 300 ps delay times, respectively) are indicated. The spectrum B is mainly due to the S_1 state of 9-CA because of the relative low concentration of DMA (ca. 0.1 M), while the spectrum C is mainly due to the $(9\text{-CA})^-\cdots DMA^+$ ion pair which shows decay due to back electron transfer within 1 ns. Although this absorption spectrum of the $(9\text{-CA})^-\cdots DMA^+$ ion pair is much broader compared with the spectra of 10-CN-ADMA in polar solvents given in Fig. 4, its wavelength region agrees very well with those of 10-CN-ADMA in polar solvents, which suggests strongly that the excited 10-CN-AMDA in polar solvents should be characterized by a large intramolecular charge separation between the 9-CA and DMA moieties. The broadening of the spectrum in Fig. 5C compared to those of Fig. 4C, D, E, could be ascribed to the difference in the ion-pair structures. Namely, the π-electronic systems of 9-CN^- and DMA^+ of the ion pair in the case of Fig. 5C might be in a closer contact (presumably face to face?) than in the case of the intramolecular charge-transfer state of 10-CN-ADMA in polar solvents. This is exactly what was

derived experimentally from IEOEM, where a dipole moment in between 70 and $80 \cdot 10^{-30}$ C m has been found, which is equivalent to a charge transfer over 0.5 nm.

The band at 660 nm which is quite intense in the polar solvents, tetrahydrofuran, 1-butanol, and acetonitrile, is also contained in the spectra in cyclohexane and fluorobenzene solutions, although quite weakly. Hence, these spectra might be considered as a superposition of a 9-CA anion spectrum from a locally excited 9-CA like state. In this case, the dipole moment of the excited 10-CN-ADMA determined in cyclohexane ought to be represented very roughly by the sum of the first singlet excited state dipole moment of 9-CA[22] and of the ground state dipole moment of dimethylaniline,[26] which would amount to about $35 \cdot 10^{-30}$ C m. This value was used as an alternative value for calculating q in Table 4. It is considerably less than the experimental value reported for heptane solutions (Table 3). The difference could either be ascribed to the fact that the two molecular subunits cannot be considered isolated, or that even in heptane there is some amount of A-state emission.

The large value for μ_e in Table 3 found for fluorobenzene indicates that there is almost a full charge transfer in fluorobenzene although the S_n-S_1 spectrum is not yet the one of the ion-pair like state, as revealed in the polar solvents tetrahydrofuran, 1-butanol and acetonitrile. This means that such an ion pair like state is not yet reached in fluorobenzene, i.e. the electronic structure of the excited state is still slightly less polar.

The two state interpretation of the S_n-S_1 spectra is also in agreement with the ground state absorption spectrum, which shows a long wavelength shoulder fronting the 9-CA like first absorption band. From EOAM in this shoulder, the highyl polar ICT character of the respective FC-state was derived as described already. Figure 6 shows the ground state absorption spectrum in cyclohexane between 20 and $40 \cdot 10^5$ m^{-1}. The absorption bands around 32 and $38 \cdot 10^5$ m^{-1} might be due to transitions to the same excited states as those reached by the S_n-S_1 absorption processes in cyclohexane at 570 nm ($17.5 \cdot 10^5$ m^{-1}) and 870 nm ($11.5 \cdot 10^5$ m^{-1}), which can be seen if a small stabilization of about 1 to $1.5 \cdot 10^5$ m^{-1} of the equilibrium excited state with respect to the first FC-excited state at $22.5 \cdot 10^5$ m^{-1} is taken into account.

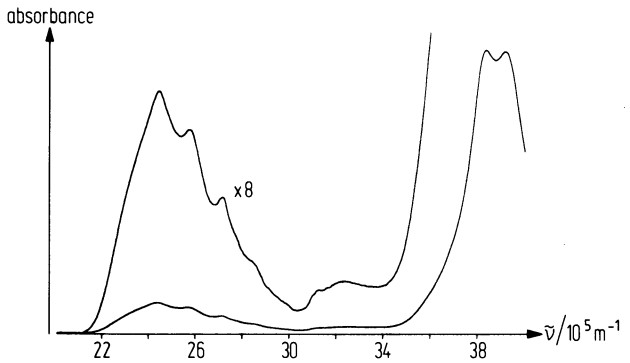

Fig. 6. Ground state absorption spectrum of 10-CN-ADMA in cyclohexane at 298 K. Concentration was 1.2 10^{-5} mol dm^{-3}.

Concluding Remarks. The absorption and fluorescence behavior of 10-CN-ADMA can be well-understood assuming two nearby electronic states, a very polar state A and a less polar state B. From the electric field dependence of these spectra, equilibrium excited state dipole moments μ_e as well as Franck-Condon excited state dipole moments μ_e^{FC} could be determined. The values from these measurements fit well to the results from solvent shift measurements of the fluorescence[17] and to those from the solvent dependent S_n-S_1 spectra. The very solvent dependent S_n-S_1 spectra as well as the levelling off of the μ_e^{-1} values discussed above (Discussion Assuming Two Emitting Species or States) make the two state model strongly favoured.

The observed dipole moment μ_e°(A) of about $80 \cdot 10^{-30}$ C m is in agreement with the picture of about one-electron charge transfer between the 9-cyanoanthracene and the dimethylaniline moieties.

The agreement between μ_e° and μ_e^{oFC} although within large errors, shows that there does not occur any dramatic change of the dipole moment after excitation, as had been one of the working hypotheses at the beginning of the application of the TICT model[29,30] to various compounds. Hence, no decision can be made whether there is a conformational change of 10-CN—ADMA after excitation to a TICT state, or whether there is simply an intramolecular charge transfer state.

The Mainz group gratefully acknowledges financial support by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft. The present work was also partly supported by Grants-in-Aid (Nos. 5843003, 60040059, 61040046, and 61123008) from the Japanese Ministry of Education, Science and Culture to N.M.

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