Synthesis and Spectroscopic Properties of Some Compounds Related to Benzenamine-4-(9-anthryl)-N,N-dimethyl [ADMA]

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The synthesis of several compounds related to ADMA are described in detail. These compounds are characterized by their mass, NMR, and IR-spectra. In addition, the solvent dependent shift of the fluorescence as well as the effect of an electric field on the fluorescence have been measured. The results are in agreement with a two-state model assuming the simultaneous fluorescence from a weakly polar and a highly polar state with dipole moment μ. μ^2/a^3 (a is Onsager's radius) has been determined from both effects. The results are in good agreement with an excited state dipole moment of about $60 \cdot 10^{-30}$ Cm, in the polar state.

1. Introduction

The fluorescence behaviour of benzenamine-4-(9-anthryl)-N,N-dimethyl – the so-called ADMA – has been studied in some detail in the literature [1–14]. The solvent polarity structure and shift of the fluorescence band which doesn't show any similarity with the absorption spectrum was first discussed in terms of an intramolecular charge transfer (ICT) excited state perhaps accompanied by a change of the conformation by Okada et al. [5].

Grabowski et al. [8] and Siemiarczuk et al. [6, 11, 14] show that the kinetic behaviour of ADMA and some related compounds can be understood at least in polar solvents if a spontaneous formation of a twisted intramolecular charge transfer (TICT) state after excitation is assumed, as was originally introduced in 1973 [15] to describe the fluorescence behaviour of benzenamine-4-cyano-N,N-dimethyl (DMABN).

From a comparison of the behaviour of ADMA and some sterically hindered derivatives [8] it is derived that most probably the anthryl moiety is perpendicular to the phenyl plane, in the TICT excited state. Baumann et al. [7] have shown that the behaviour of ADMA and some related compounds might also be due to reaction field induced polarizability effects with only one conformer that doesn't necessarily show TICT formation. Nevertheless, an interpretation of their experimental results in terms of the TICT model has been shown to be possible, too [9]. Hence it seems to us that up to now there are a lot of experimental results that can be explained by conformational changes or (and) by solvent polarity induced effects, like solvent assisted level crossing without conformational changes as Lippert first had proposed for DMABN [16].

Since in such cases sterically more or less fixed derivates could give more insight, two new molecules have been synthesized namely benzenamine-4-(9-anthryl)-N,N,2,6-tetramethyl (2,6-DM-ADMA) where the rotation of the dimethylamino group is hindered and benzenamine-4-(9-anthryl)-N,N,2,3,5,6-hexamethyl (TM – ADMA) where the rotation of both the anthryl and dimethylaniline group is hindered; hence these moieties are twisted out of the phenyl plane. In addition, benzenamine-4-(9,10-cyanoanthryl)-N,N-dimethyl (10-CN-ADMA) has been synthesized as a model compound where the polar state should be energetically lowest already in non-polar solvents. Fig. 1 shows the class of molecules to be discussed in this communication.

II. Compounds

All reactions were carried out in an Argon-atmosphere (99.996%; OXISORB-apparatus, MESSER-GRIESHEIM) in order to prevent autooxidation reactions of the amines, respectively other side reactions of the organometallic intermediates.

The ^{1}H- and ^{13}C-NMR-spectra were taken on a BRUKER WH 90 NMR spectrometer, the 70 eV El-mass-spectra on a Varian CH 7A mass spectrometer

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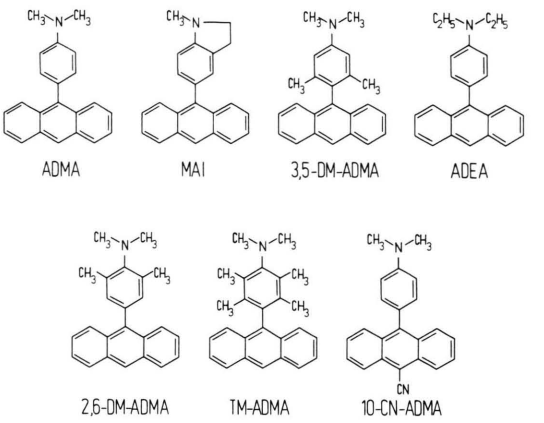

Fig. 1. Structure of the molecules considered in this paper. ADMA: benzenamine-4-(9-anthryl)-N,N-dimethyl MAI: 1-H-indole, 5-(9-anthryl)-2,3-dihydro-1-methyl, 3,5-DM-ADMA: benzenamine-4-(9-anthryl)-N,N,3,5-tetramethyl. ADEA: benzenamine-4-(9-anthryl)-N,N-diethyl 2,6-DM-ADMA: benzenamine-4-(9-anthryl)-N,N,2,6-tetramethyl. TM-ADMA: benzenamine-4-(9-anthryl)-N,N,2,3,5,6-hexamethyl 10-CN-ADMA: benzenamine-4-(9,10-cyanoanthryl)-N,N-dimethyl.

and the IR-spectra on a JASCO-IRA-2 infrared spectrometer.

Microanalyses were performed by the Analytical Laboratories Prof. Dr. H. Malissa, Engelskirchen, West Germany.

TLC experiments for analytical purposes were carried out on commercial TLC-plates (see below) by the CAMAG VARIO-KS-chamber technique, respectively in CAMAG twin through chambers. LC purifications (see below) were mostly performed by the DCC-technique according to Loev [17].

II.1. ADMA

The preparation of ADMA described by Barnett et al. [18] was modified in order to increase the yield of this compound.

To a stirred suspension of 28 g (0,085 mole) of 9,10-dibromo-9,10-dihydroanthracene [18] in 60 ml chloroform at −20 °C a solution of 24 g (0,198 mole) N,N-dimethylaniline in 30 ml chloroform was dropped within 20 min. The suspension was still kept at −20 °C for two hours, then warmed up to room temperature and stirred for further 17 h.

The product was sucked off and washed several times with 2*n* sodium hydroxide and water to remove the dimethylaniline-hydrobromide.

Yield: 18.3 g (73%) (Lit. [18]: 40%);

Purification: 1. DCC: stat. phase: alumina, neutral, act. III mob. phase: cyclohexane (abs); 2. recrystallization from toluene.

Purity test: TLC: stat. phases: alumina, silica mob. phases: cyclohexane, toluene, dichloromethane, chloroform.

mp: 258 °C
$C_{22}H_{19}N$

calcd:	C 88.85	H 6.44	N 4.71
found:	C 88.60	H 6.51	N 4.82

Molar mass: 297.4 g mole^{-1}

The substance was further identified by means of mass-spectral and infrared data and a mixed melting point with an authentic sample.

II.2. Benzenamine-4-(9-anthryl)-N,N-diethyl (ADEA)

The preparation of this compound was performed strictly analoguous to that of ADMA given above.

Hence, from 29.2 g (0.196 mole) of freshly destilled N,N-diethylaniline and 32.8 g (0.100 mole) 9,10-dibromo-9,10-dihydroanthracene [19] 19.5 g (59%) of crude ADEA could be obtained.

Purification: 1. DCC: same conditions as ADMA;
2. Recrystallization from ethanol.
mp: 197−198 °C
$C_{24}H_{23}N$

Calcd:	C 88.57	H 7.13	N 4.30
Found:	C 88.48	H 7.12	N 4.27

Molar mass: 325.46 g mole^{-1}

Mass spectrum:

326 ($M+1^+$, 51), 325 (M^+, 100), 324 ($M-1^+$, 7), 311 (45), 310 (M^+-CH_3, 100), 282 (22), 281 (M^+-CH_3-Et, 72), 253 (M^+-NEt_2, 49), 254 (12), 252 (73), 251 (12), 250 (16), 155 (43), 141 (25), 126 (13).

IR (KBr): $\tilde{\nu}$/cm^{-1} = 3028 (w, CH-aromat.), 2970 (m, sh, CH_3-aliphat.), 2870 (w, CH_2-aliphat.), 1603 (s, sh, C=C$^-$ aromat.), 1515 (s, sh, C=C-aromat.), 1435 (m), 1410 (s), 1392 (m), 1370 (m), 1335 (s, C−N-aromat., tert.), 1264 (s), 1200 (s, sh, aromat. − 1,4-subst.), 1155 (w), 1140 (w), 1110 (m), 890 (s), 850 (s), 810 (m), 795 (m), 735 (ss, sh);

^{1}H-NMR(CD_2Cl_2): δ/ppm = 1.28 (t, J = 8 Hz, 6 H, $-CH_3$), 3.49 (q, J = 8 Hz, 4 H, N−CH_2−), 6.84−7.54 (m, 8 H, other anthracene protons), 7.81−8.10 (m, 4 H, phenyl protons), 8.46 (s, 1 H, 10-position anthracene).

II.3 Benzenamine-4-(9,10-bromoanthryl)-N,N-dimethyl (10-Br-ADMA)

To a stirred solution of 1.49 g (5 mmole) ADMA in 40 ml of dichloromethane at ambient temperature, small portions of 2.05 g (5 mmole) 2,4,4,6-tetrabromo-2,5-cyclohexadiene-1-one [20] were added over a three hours period. The reaction mixture was then shaken with 2 n sodium hydroxide, the organic layer separated and washed with water. After drying over anhydrous sodiumsulfate, the solvent was removed in vacuo.

Yield: 1.49 g (80%).

Purification: 1. DCC: stat. phase: alumina, act. III; mob. phase: cyclohexane/toluene (70:30).
2. Recrystallization from toluene.
Purity test: TLC: stat. phase: alumina 60, silica: mob. phase: cyclohexane/toluene (70:30).

mp: 280–282 °C (dec.)

$C_{22}H_{18}BrN$

Calcd:	C 70.22	H 4.82	N 3.72	Br 21.24
Found:	C 70.05	H 4.94	N 3.61	Br 21.39

Molar mass: 376.29 g mole^{-1}

Mass spectrum: 378 (21), 3.77 (M + 1$^+$, 96), 376 (M$^+$, 35), 375 (M − 1$^+$, 100), 374 (10), 253 (13), 252 (M$^+$ − Br − N(CH$_3$)$_2$, 39), 250 (10), 188 (12), 187 (14), 126 (25), 125 (14).

IR(KBr): $\tilde{\nu}$/cm^{-1} = 1580 (s, C = C aromat.), 1480 (s, aromat.), 1330 (s, C−N tert.), 1210 (m, aromat., 1,4-subst.), 1190 (m), 1175 (m), 928 (s), 873 (s, benzene, 1,4-subst.), 810 (s), 783 (m), 755 (s);

^{1}H-NMR(CDCl$_3$): δ/ppm = 8.54 (d, 2 H, 1,8-anthracene), 7.35–7.84 (m, 6 H, anthracene), 6.89–7.30 (m, 4 H, phenyl), 3.08 (s, 6 H, N-methyl);

^{13}C-NMR(CDCl$_3$): δ/ppm = 40.54 (N-methyl), 112.16 (C-2,6-phenyl), 121.68, 125.16, 125.22, 126.85, 127.76, 130.36, 131.66, 131.92 (anthracene, phenyl), 149.12 (C-1, phenyl).

II.4 10-CN-ADMA

A stirred mixture of 0.76 g (2 mmole) 10-Br-ADMA, 0.36 g Cu(I)cyanide (4 mmole), 30 ml dimethylformamide (abs) and 2 ml pyridine (abs) was heated to 140 °C over a 24 h period. The hot reaction mixture was then poured into a stirred, ice-cooled solution of 5 g (0.1 mole) sodiumcyanide in 100 ml water. The water phase was extracted (1 h) with chloroform and the organic phase washed with 5% sodiumcyanide solution and water. After drying over anhydrous sodiumsulfate, the solvent was removed in vacuo (traces of DMF required high vacuum application).

Yield: 0.5 g (78%). Applying the tenfold molar amount of Cu(I)cyanide raised the yield up to 95%.

Purification: 1. DCC: stat. phase: alumina, neutral, act. III, mob. phase: toluene (abs);
2. Recrystallization from toluene (abs).

Purity tests: TLC: stat. phase: alumina, silica.
Mob. phase: toluene (abs), toluene/cyclohexane (abs), (70:30).

$C_{23}H_{18}N_2$

Calcd.	C 85.68	H 5.63	N 8.69
Found:	C 85.50	H 5.81	N 8.37

Molar mass: 322.41 g mole^{-1}

Mass spectrum: 323 (26), 322 (M$^+$, 100), 278 (M$^+$−N(CH$_3$)$_2$, 22), 277 (23), 251 (M$^+$−N(CH$_3$)$_2$−HCN, 4), 162 (M^{2+}/2, 11), 97 (11), 71 (13), 69 (14), 57 (21), 55 (15), 43 (14).

IR(KBr): $\tilde{\nu}$/cm^{-1} = 2212 (s, C≡N), 1608 (s, C=C-aromat.), 1521 (s), 1484 (m, aromat.), 1359 (s, C−N tert.), 1206 (s, aromat., 1,4-subst.), 813 (s, 1,4-subst.), 770 (s), 760 (s), 608 (s);

^{1}H-NMR(CD$_2$CL$_2$): δ/ppm = 8.41 (d, 2 H, 1,8-anthracene), 7.02–7.85 (m, 10 H, anthracene, phenyl), 3.09 (s, 6 H, N-methyl).

II.5 Benzenamine-4-bromo-N,N,2,3,5,6-hexamethyl

A mixture of 11.4 g (50 mmole) benzenamine-4-bromo-2,3,5,6-tetramethyl [21], 15.0 g (0.5 mole) paraformaldehyde and 150 ml formic acid (p.a. 98–100%) was stirred at a temperature of 100 °C over a period of 24 h.

The still hot reaction mixture was poured into a rapidly stirred, ice-cooled solution of 250 g sodiumhydroxide and 90 g sodiumsulfite in 1200 ml water. Stirring was continued for 1.5 h.

The solution was then extracted with ether, the organic phase washed with a 5% sodiumsulfite solution and water and dried over anhydrous sodiumsulfate. Evaporation of the solvent in vacuo yielded 11.72 g (91%) of a colourless powder.

Purification: DCC: stat. phase: alumina TSC, act. III.
Mob. phase: cyclohexane (abs).

Purity tests: TLC: stat. phases: alumina, silica.
Mob. phases: cyclohexane, toluene (abs).
mp: 85–86 °C.

$C_{12}H_{18}BrN$

Calcd.:	C 56.26	H 7.08	N 5.47	Br 31.19
Found:	C 56.36	H 7.12	N 5.41	Br 31.27

Molar mass: 256.19 g mole^{-1}

Mass spectrum: 258 (15), 257 (M + 1$^+$, 99), 256 (M$^+$, 54), 255 (M − 1$^+$, 100), 254 (41), 243 (12), 242 (97), 241 (M$^+$ − CH$_3$, 17), 240 (M − 1$^+$ − CH$_3$, 99), 226 (23), 225 (M$^+$ − 2*x*CH$_3$, 6), 224 (22), 216 (M − 1$^+$ − N(CH$_3$)$_2$, 7), 161 (M$^+$ − Br − CH$_3$, 17), 160 (20), 159 (20), 146 (M$^+$ − Br − 2 *x*CH$_3$, 22), 145 (25), 144 (17), 132 (17), 131 (M$^+$ − Br − 3 *x* CH$_3$, 19), 130 (12), 117 (36), 116 (M$^+$ − Br − 4*x*CH$_3$, 16), 115(28), 91($C_7H_7^+$, 33), 77(19), 65(13), 44(30), 42(17), 41(13).

IR(KBr): $\tilde{\nu}$/cm^{-1} = 2900 − 2760(m, br, CH_3−), 1475−1370(m, very br C=C-aromat., N−CH_3), 1328(m, C−N-tert., aromat.), 1230(w), 1190(m), 1060(m), 1000(m), 860(m);

^{1}H-NMR($CDCl_3$): δ/ppm = 2.87(s, 6H, N−$(CH_3)_2$), 2.46(s, 6H, 2,6-methyl), 2.32(s, 6H, 3,5-methyl).

II.6 TM-ADMA

All attempts to prepare this compound analoguously to the conventional method [18, 19] or by application of the Grignard-compound failed.

Additionally to the applicated inert gas atmosphere (see above) all reagents must be carefully dried and the employed apparatus must be free of any traces of adsorbed moisture, achieved by repeated heating (200 °C) in the argon stream. The used ether is refluxed over $LiAlH_4$ for three hours and directly destilled into the reaction vessel. A solution of 7.69 g (30 mmole) benzenamine-4-bromo-N,N,2,3,5,6-hexamethyl (dried over KOH in high vacuum for 24 h) in 20 ml of ether is dropped to a stirred suspension of 0.7 g chopped lithium wire (100 mmole) in 50 ml ether over a period of 30 min so that the reaction mixture remains gently boiling. After additional refluxing over 45 min a greenish opalescent solution is obtained and 30 ml of ether are destilled in. Then, 1.94 g (10 mmole) of anthrone (dried over P_2O_5 in high vacuum over 24 h) are placed in a solid extractor (30 ml content) and added to the still heated reaction mixture (bath temperature 50 °C) by destillation of ether into the extractor and solving the anthrone by additional heating (hot air gun) over a period of 1.5 h. This method has turned out to be necessary because anthrone is extremely insoluble in cold ether and in order to keep the amount of ether as small as possible (water traces!).

The reaction mixture is then immediately poured on ice, first acidified (2 *n* H_2SO_4) and then alcalized by addition of NaOH (stirring and externally cooling by ice/water). Then the mixture is extracted with ether, the etheral solution washed with water, filtered (hereby 0,354 g of 9,10-anthraquinone can be isolated), dried over anhydrous sodiumsulfate and the solvent removed in vacuum.

Yield: 6.7 g solid (more than 100%).

Purification: 1. LC: stat. phase: alumina 90, neutral, act. III, mob. phase: cyclohexane (abs).

From 13.4 g raw material the following products were isolated and identified.

7.56 g benzenamine-N,N,2,3,5,6-hexamethyl, mp: 53−55 °C; 3.69 g of a mixture of the desired compound and a by-product (see below); 0.59 g of 9,10-anthraquinone.

Recrystallization of the mixture from ethanol yielded still mixed crystals (mp: 128 °C). Furthermore a separation by LC was impossible. Separation was finally achieved by preparative thin layer chromatography (PTLC):

2. PTLC: stat. phase: silica 40, mob. phase: cyclohexane/NH_3 (conc.), (99:1) additional conditions: 30−40 mg of the mixture could be separated one run.

In a typical PTLC experiment starting with 210 mg of the mixture (7 runs), 142 mg of pure TM-ADMA and 54 mg of the pure by-product could be isolated.

3. Recrystallization: TM-ADMA: from methanol. mp: 189 °C by-product: from ethanol/H_2O (2:1). mp: 127 °C (identification see below).

Purity test: TLC: stat. phase: silica.

Mob. phase: Cyclohexane/NH_3 (conc.) (99:1).

$C_{26}H_{27}N$

Calcd:	C 88.34	H 7.70	N 3.96
Found:	C 88.18	H 7.77	N 3.96

Molar mass: 353.51 g mole^{-1}

Mass spectrum: 355(M + 1$^+$, 24), 354(M$^+$, 31), 353(M − 1$^+$, 100), 340(12), 339(M$^+$−CH_3, 14), 338(M−1$^+$−CH_3, 51), 323(M−1$^+$−2*x*CH_3, 12), 322(18), 308(M−1$^+$−3*x*CH_3, 8), 294(M$^+$−4*x*CH_3, 14), 293(M−1$^+$−4*x*CH_3, 10), 279(M−1$^+$−5*x*CH_3, 17), 263(M$^+$−6*x*CH_3, 3), 177(M^{2+}/2,5), 162(3), 146(3), 44($CH_3CH{=}NH_2^+$, 7);

^{1}H-NMR(CCl_4): δ/ppm = 8.37(s, 1H, 10-position anthracene), 7.87−8.03(d, 2H, 1,8-position anthracene), 7.20−7.60(m, 6H, other anthracene protons), 3.03(s, 6H, N−$(CH_3)_2$), 2.34(s, 6H, 2,6-methyl), 1.63(s, 6H, 3,5-methyl).

By-product: benzenamine-4-(9-9,10-dihydroanthryl)-N,N-2,3,5,6-hexamethyl

$C_{26}H_{29}N$

Calcd:	C 87.84	H 8.22	N 3.94
Found:	C 87.71	H 8.21	N 3.85

Molar mass: 355.51 g mole^{-1}

Mass spectrum: 357(M + 1$^+$, 4), 356(M$^+$, 28), 355(M − 1$^+$, 100), 354(10), 340(M−1$^+$−CH_3, 30), 325(M−1$^+$−2 CH_3, 14), 311(M$^+$−3*x*CH_3, 27), 310(M−1$^+$−3*x*CH_3, 6), 295(M−1$^+$−4*x*CH_3, 8), 280(M−1$^+$−5*x*CH_3, 6), 265(M−1$^+$−6*x*CH_3, 4), 179(47), 178(anthracene$^+$, 30), 162(29), 146(24), 91($C_7H_7^+$, 5), 44(CH_3−CH=NH$^+$, 7);

^{1}H-NMR($CDCl_3$): δ/ppm = 6.57−7.43(m, 8H, anthracene protons), 5.57(s, 1H, 9-position), 4.10(d, 2H, 10-position), 2.92(s, 6H, −N$(CH_3)_2$), 2.37(s, 6H, 2,6-methyl), 2.12(s, 3H, 5-methyl), 1.29(s, 3H, 3-methyl).

II.7 Benzenamine-4-bromo-N,N,2,6-tetramethyl

In contrast to the previously described method [22] methylation of benzenamine-4-bromo-2,6-dimethyl [23] by the following modified paraformaldehyde method yielded this compound free of any monoalkylated by-product.

A mixture 20 g (0.1 mole)-4-bromo-2,6-xylidine, 30 g (1.0 mole) paraformaldehyde and 100 ml formic acid (99.5%) was stirred at 95 °C over a 24 h period. The hot homogeneous reaction mixture was poured into a vigorously stirred ice-cooled solution of 150 g NaOH and 200 g $Na_2S_2O_5$ in 1100 ml water. After one hour the mixture was extracted with ether, the ether extract washed three times with an alkaline solution of $Na_2S_2O_5$ (10%), then with water and dried over Na_2SO_4. After removal of the solvent, the crude product showed no monoalkylated by-product as proven by IR-measurements and TLC experiments.

Purification: Fractionated vacuum destillation; $bp_{0.01}$: 70 °C; mp: 32 °C (lit. [19]: 32–33 °C).
Yield: 91%.

II.8 2,6-DM-ADMA

This compound was prepared exactly by the same method described above with the preparation of TM-ADMA.

6.84 g (30 mmole) of benzenamine-4-bromo-N,N,2,6-tetramethyl, 0.7 g Li and 1.94 g (10 mmole) of 9-anthrone yielded 3.6 g of crude, oily material, which contained still 0.2 g of benzenamine-N,N,2,6-tetramethyl.

Purification: 1. LC: stat. phase: alumina, neutral, act. III; mob. phase: cyclohexane (abs), toluene (abs); 2. recrystallization from ethanol.

Yield: 2.95 g (90%) colourless needles;
mp: 169 °C;
Purification tests: TLC: stat. phases: alumina, silica. Mob. phase: toluene.

In addition to the above mentioned amine, only 0.4 g of 9,10-anthraquinone was identified as a by-product. The generation of the 9,10-dihydroanthracene derivative as in the case of TM-ADMA was not observed.

$C_{24}H_{23}N$

Calcd:	C 88.57	H 7.12	N 4.31
Found:	C 88.51	H 7.23	N 4.36

Molar mass: 325.45 g $mole^{-1}$
Mass spectrum: 326 ($M+1^+$, 26), 325 (M^+, 100), 324 ($M-1^+$, 11), 310 (M^+-CH_3, 22), 266 (17), 265 (17), 163 (9), 162 (11), 44 (6).

IR(KBr): $\tilde{\nu}/cm^{-1}$ = 3021 (w, CH-aromat.), 2941, 2890, 2833, 2763 (w, CH_3), 1610 (s, C=C-aromat.), 1488 (s), 1470 (s), 1431 (m), 1404 (m), 1364 (s), 1357 (m), 1115 (s), 1009 (s), 890 (s), 885 (s), 876 (s), 843 (s), 792 (s), 730 (m), 660 (m), 649 (m).

^{1}H-NMR(CCl_4): δ/ppm = 2.46 (s, 6 H, 2,6-methyl), 3,05 (s, 6 H, N-dimethyl), 7.02 (s, 2 H, 3,5-phenyl), 7.20–8.00 (m, 8 H, anthracene), 8.34 (s, 1 H, 10-anthracene).

II.9 Benzenamine-4-(9-anthryl)-N,N,3,5-tetramethyl

(3,5-DM-ADMA) and 1-H-indole,5-(9-anthryl)-2,3-dihydro-1-methyl (MAI) have been supplied by Z. R. Grabowski and have been used without further purification.

III. Results

III.1 Absorption and Fluorescence Spectra

The absorption and fluorescence spectra of the new compounds 2,6-DM-ADMA, TM-ADMA and 10-CN-ADMA and of ADMA are shown in Figs. 2 to 5, in some selected solvents. It is seen that 2,6-DM-ADMA and 10-CN-ADMA behave similar to all known compounds within this group [6] but TM-ADMA displays two distinct fluorescence bands, the relative intensities of which are strongly solvent polarity dependent. The longwavelength fluorescence band is strongly enhanced and redshifted with increasing solvent polarity, very similar to the solvent shift of the broad fluorescence band observed with all other known compounds of this class, e. g. with 2,6-DM-ADMA, too. Thus, for the first time the existence of two fluoresceing states could be shown directly with a molecule of this class of compounds [24].

III.2 Solvent Shift Measurements

The solvent dependent shift of an isolated fluorescence band can be used to evaluate μ^2/a^3, where μ is the dipole moment of the considered molecule in its fluorescent excited state and a is Onsager's

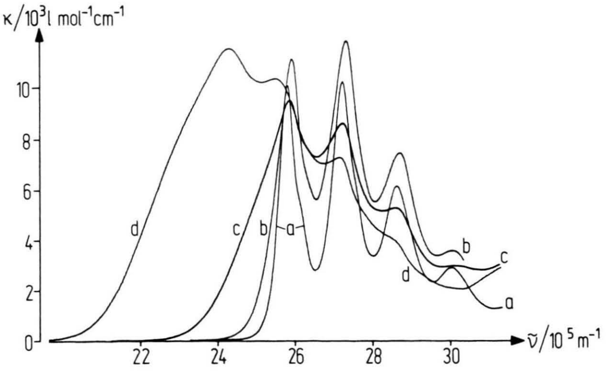

Fig. 2. Absorption spectra of a) TM-ADMA, b) 2,6-DM-ADMA, c) ADMA, and d) 10-CN-ADMA in dioxane, at 298 K.

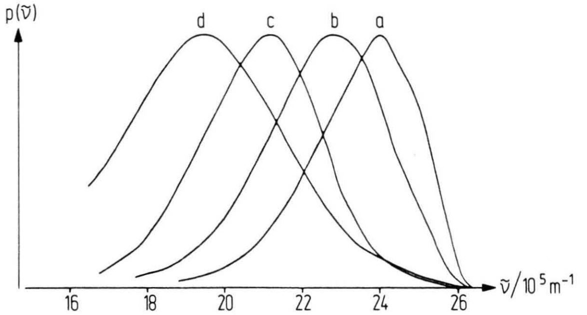

Fig. 3. Fluorescence spectra of 2,6-DM-ADMA in a) 2-methylbutane, b) di-isopropylether, c) fluorobenzene, and d) n-butanol, at 298 K.

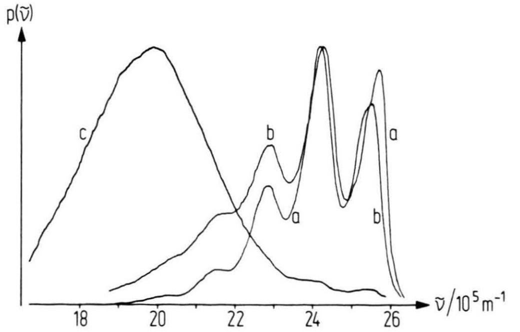

Fig. 4. Fluorescence spectra of TM-ADMA in a) cyclohexane, b) diisopropylether, and c) fluorobenzene, at 298 K.

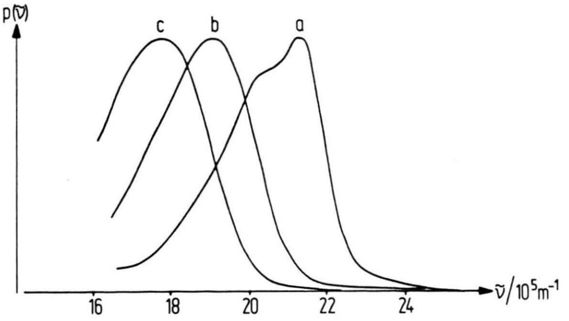

Fig. 5. Fluorescence spectra of 10-CN-ADMA in a) methylcyclopentane, b) di-isopropylether, and c) fluorobenzene, at 298 K.

interaction parameter [25] which is given approximately by the radius of a sphere circumscribed around the solute molecule. Neglecting polarizability effects and assuming the excited state life time sufficiently larger than the solvent reorientation relaxation times, the solvent dependence of the wavenumber $\tilde{\nu}_{\max}$ of the fluorescence band maximum can be represented [26] by

$$\tilde{\nu}_{\max} = \text{const} - [(\boldsymbol{\mu} - \boldsymbol{\mu}_g)\, \boldsymbol{\mu}\, g - (\boldsymbol{\mu} - \boldsymbol{\mu}_g)^2 g'/2]/(2\pi \varepsilon_0 h c a^3)\,. \tag{1}$$

ε_0 is the permittivity of the vacuum, h Planck's constant and c the velocity of light. Within the framework of the Onsager model, the functions g and g' are defined as

$$g = (\varepsilon - 1)/(2\varepsilon + 1)\,, \tag{2}$$

$$g' = (n^2 - 1)/(2n^2 + 1)\,. \tag{3}$$

ε its dielectric constant and n the refractive index of the solvent.

For all compounds except 10-CN-ADMA the ground state dipole moment μ_g may be taken negligibly small compared to μ, according to the results from [7]. Then

$$\tilde{\nu}_{\max} = \text{const} - (g - g'/2)\, \mu^2/(2\pi \varepsilon_0 h c a^3)\,. \tag{4}$$

If it is taken into account that g' does not change very much with differently polar solvents, another simplified version of (1) can be used:

$$\tilde{\nu}_{\max} = \text{const} - g\,(\boldsymbol{\mu} - \boldsymbol{\mu}_g)\, \boldsymbol{\mu}/(2\pi \varepsilon_0 h c a^3)\,. \tag{5}$$

Figures 6 and 7 show plots of $\tilde{\nu}_{\max}$ versus $(g - g'/2)$ and g, respectively. At least with ADMA, ADEA and very distinctly with 2,6-DM-ADMA a non-linear curve is observed which might be approximated by a straight line in the range of medium and highly polar solvents. This is in best agreement with the results published for ADMA by Mataga et al. [5] already in 1976.

All existing models assume structural changes and/or two or more emitting states/species in order to describe this other observations. Beyond a certain dielectric constant, one emitting species/state with sufficiently rigid structure then might be assumed. Thus, according to (4) or (5), from a linear regression analysis of $\tilde{\nu}_{\max}$ with respect to $(g - g'/2)$ or g, in solvents with $\varepsilon > 4$, μ^2/a^3 can be determined in the solute's respective emitting state.

Table 1 represents the results for μ^2/a^3 determined according to (4) and the results for $(\boldsymbol{\mu} - \boldsymbol{\mu}_g)\,\boldsymbol{\mu}/a^3$ with 10-CN-ADMA according to (5) since $\mu_g = 20 \cdot 10^{-30}$ Cm is not small compared to μ.

In order to estimate the parameter a, $\mu = 60 \cdot 10^{-30}$ Cm ($80 \cdot 10^{-30}$ Cm for 10-CN-ADMA) is assumed as a roughly estimated average value, based on the experimental results in polar solvents [7, 27]. The resulting values for the parameter a^3 are in good agreement with the molecular dimensions of the solutes.

III.3. Electro Optical Emission Measurements (EOEM) with Superimposed Fluorescence Bands

With EOEM, the photon flux $p^{\mathrm{E}}(\tilde{\nu}, \varphi)$ from solute molecules in an external electric field E_{a} is observed at the wavenumber $\tilde{\nu}$ and through a polarizer that defines the angle φ between the electric field vector of the polarized light and E_{a}. Experimentally, the following dependence of $p^{\mathrm{E}}(\tilde{\nu}, \varphi)$ on E_a is observed [28]:

$$p^{\mathrm{E}}(\tilde{\nu}, \varphi) = p(\tilde{\nu})\,[1 + y(\tilde{\nu}, \varphi)\,E_{\mathrm{a}}^2]\,. \tag{6}$$

Table 1. μ^2/a^3 and the parameter "*a*" from solvent shift measurements. The errors are derived from the standard errors of the respective regression coefficients. For the determination of "*a*" see text.

	$(\mu^2/a^3)/10^{-30}\,\mathrm{C^2\,m^{-1}}$	$a/10^{-10}$ m
ADMA	18.8 ± 1.9	5.8
ADEA	21.0 ± 2.9	5.6
2,6-DM-ADMA	33.3 ± 5.1	4.8
3,5-DM-ADMA	22.7 ± 1.8	5.4
TM-ADMA	34.0 ± 4.2	4.7
MAI	19.1 ± 1.9	5.7
10-CN-ADMA [a]	22.3 ± 1.7	6.0

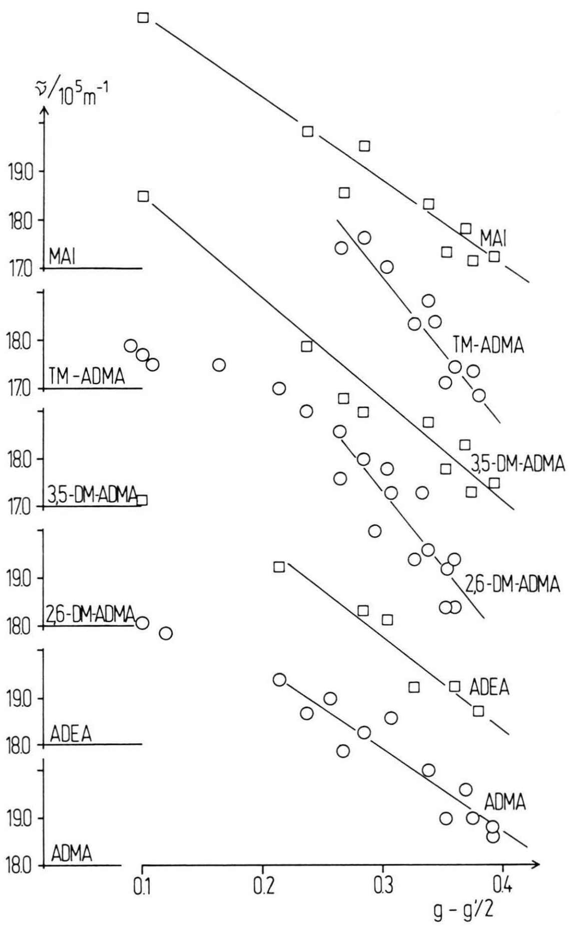

Fig. 6. Plot of the wavenumber of the fluorescence maximum versus the solvent parameter $g - g'/2$, for several compounds related to ADMA.

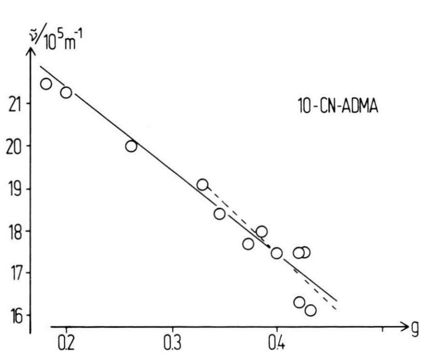

Fig. 7. Plot of the wavenumber of the fluorescence maximum versus the solvent parameter g, for 10-CN-ADMA.

Thus a set of values $y(\tilde{\nu}, \varphi)$ can be determined from experiment [29]. Using a suitable model [30], a respective molecular model quantity $Y(\tilde{\nu}, \varphi)$ can be calculated. The theory has been given for a homogeneous transition between two electronic states of one solute species [6], where

$$Y(\tilde{\nu}, \varphi) = L_0 + E\,(3\cos^2\varphi - 1)/30 + [F\,(2\cos^2\varphi + 1) + G\,(3\cos^2\varphi - 1)]\, t(\tilde{\nu}) \,. \quad (7)$$

$t(\tilde{\nu})$ is proportional to the first derivative of the respective fluorescence band. It is given in [31] but is not needed in the present paper explicitly. Terms proportional to the second derivative have been neglected as usually small compared to the terms in (7). L_0 is a constant depending on the excitation condition.

$$E = f_e^2 \beta^2 [3\,(\boldsymbol{m}\boldsymbol{\mu}')^2 - (\boldsymbol{\mu}')^2] \,, \quad (8)$$

$$F = f_e^2 \beta\, \boldsymbol{\mu}' \Delta\boldsymbol{\mu} \,, \quad (9)$$

$$G = f_e^2 \beta\, (\boldsymbol{m}\boldsymbol{\mu}')\, (\boldsymbol{m}\Delta\boldsymbol{\mu}) \,, \quad (10)$$

where

$$\beta = (k\,T)^{-1} \,. \quad (11)$$

f_e connects the externally applied electric field E_a to the field effective in solution; for details see [30].

$$f_e = 3\,\varepsilon/(2\,\varepsilon - 1) \,. \quad (12)$$

$\boldsymbol{m}$ is a unit vector in the direction of the transition moment involved in the fluorescence process, $\boldsymbol{\mu}'$ is the total dipole moment of the solute in it's fluorescent excited state, effective in solution and $\Delta\boldsymbol{\mu}$ is essentially the change of the effective dipole moment with the emission process [28].

In the case of the class of molecules considered here, $\boldsymbol{\mu}'$ and $\Delta\boldsymbol{\mu}$ are parallel and in the direction of $\boldsymbol{m}$. Hence

$$E = 2 f_e^2 \beta^2 (\mu')^2 \,, \quad (13)$$

$$F = G = f_e^2\, \beta\, \mu' \Delta\mu \,. \quad (14)$$

For an isolated transition that is with one fluorescence band of a single species, one has

$$y(\tilde{\nu}, \varphi) = Y(\tilde{\nu}, \varphi) \,. \quad (15)$$

Hence, from experiment, finally μ' and $\mu' \Delta\mu$ can be determined through a regression analysis according to (7), with (13) and (14), but only if one isolated transition of one species is considered. Consider now two superimposed fluorescence spectra $p_A(\tilde{\nu})$ and $p_B(\tilde{\nu})$, one arising from a polar state A and the other from a non-polar state B, as to be assumed if the TICT model [15] were to be applied to describe the effects observed with this class of molecules. Then the whole photon flux $p(\tilde{\nu})$ is superposition of both, with (6):

$$p(\tilde{\nu}) = p_A(\tilde{\nu}) + p_B(\tilde{\nu}) + [p_A(\tilde{\nu})\, Y_A(\tilde{\nu}, \varphi) + p_B(\tilde{\nu})\, Y_B(\tilde{\nu}, \varphi)] f_e^2 E_a^2 \,. \quad (16)$$

If the dipole moments of the state B and of the ground state are taken to be zero, which is valid in good approximation for the purpose in this communication [7], (16) simplifies to

$$p^E(\tilde{\nu}, \varphi) = p_A(\tilde{\nu}) + p_B(\tilde{\nu}) + p_A(\tilde{\nu})\, Y_A(\tilde{\nu}, \varphi) f_e^2 E_a^2 \,. \quad (17)$$

Or with

$$p(\tilde{\nu}) = p_A(\tilde{\nu}) + p_B(\tilde{\nu}) : \quad (18)$$

$$p^E(\tilde{\nu}, \varphi) = p(\tilde{\nu})\, [1 + Y_A(\tilde{\nu}, \varphi) f_e^2 E_a^2 p_A(\tilde{\nu}) / (p_A(\tilde{\nu}) + p_B(\tilde{\nu}))] \,. \quad (19)$$

By comparison with (6), a set of values

$$y(\tilde{\nu}, \varphi) = Y_A(\tilde{\nu}, \varphi)\, p_A(\tilde{\nu}) / (p_A(\tilde{\nu}) + p_B(\tilde{\nu})) \quad (20)$$

can be determined experimentally.

Obviously, $Y_A(\tilde{\nu}, \varphi)$ cannot be determined from the measured $y(\tilde{\nu}, \varphi)$ as long as the superimposed spectra are not known separately.

Nevertheless, at least the ratio

$$q = y(\tilde{\nu}, \varphi = 0°) / y(\tilde{\nu}, \varphi = 90°) = Y_A(\tilde{\nu}, \varphi = 0°) / Y_A(\tilde{\nu}, \varphi = 90°) \quad (21)$$

can be determined. Then from (7) follows $q = 2$ at the maximum $\tilde{\nu}_{A,\max}$ of the A-fluorescence, since at $\tilde{\nu}_{A,\max}$ one has

$$t_A(\tilde{\nu}_{A,\max}) = 0 \,.$$

This would equally be valid for a minimum, but with ICT or TICT fluorescence bands only one maximum is expected, just as shown by TMADMA. Hence, even if there were a superposition of two bands from a polar and a non-polar state, the maximum $\tilde{\nu}_{A,\max}$ of the polar band can be detected by simply finding that wavenumber where

$$y(\tilde{\nu}, \varphi = 0°) = -2\, y(\tilde{\nu}, \varphi = 90°) \,. \quad (22)$$

This $\tilde{\nu}_{EOEM} = \tilde{\nu}_{A,\max}$ then may be compared with the total fluorescence band maxima $\tilde{\nu}_{\max}$ revealed in polar solvents, what can be considered pure A-

Table 2. $\tilde{\nu}_{\mathrm{EOEM}}/10^5\,\mathrm{m}^{-1}$ of the maximum of an assumed hidden A-fluorescence. For comparison, the maxima of the observed broad fluorescence are given in brackets.

	ADMA	ADEA	2,6-DM-ADMA	3,5-DM-ADMA	MAI	10-CN-ADMA
heptane	22.7 (23.0)				22.6	
cyclohexane	21.9 (23.1)	22.2 (23.1)		22.4 (23.5)		21.1 (21.3)
di-amylether	21.8	21.7	22.3		20.7	
di-n-propylether	22.0 (21.9)	21.4 (21.7)	22.0 (23.0)		20.1 (20.4)	19.8 (20.1)
dioxane	21.1 (21.0)			19.0 (19.4)	18.7 (19.6)	
fluorobenzene	20.4 (20.7)	20.3 (20.5)	20.8 (21.1)	18.9 (19.1)	17.9	17.5 (17.7)

Table 3. μ^2/a^3 determined from the solvent shift of $\tilde{\nu}_{\mathrm{EOEM}}$.

	$(\mu^2/a^3)/10^{-30}\,\mathrm{C}^2\,\mathrm{m}^{-1})$
ADMA	8.9 ± 3.2
ADEA	12.1 ± 2.8
2,6-DM-ADMA	17.9 ± 5.2
3,5-DM-ADMA	21.7 ± 2.5
MAI	25.7 ± 4.0
10-CN-ADMA [a]	22.2 ± 8.7

fluorescence, approximately, since the amount of B-fluorescence is negligible in these solvents.

Table 2 displays the values of $\tilde{\nu}_{\mathrm{EOEM}}$ determined this way. The values given in brackets are the maxima of the observed broad fluorescence bands. It should be noted here, that a direct comparison of $\tilde{\nu}_{\mathrm{EOEM}}$ and $\tilde{\nu}_{\max}$ is possible approximately only, since with EOEM according to the used model [28] the maximum of the spectrum $p(\tilde{\nu})/\tilde{\nu}^3$ is determined, which usually is red-shifted compared to the spectrum $p(\tilde{\nu})$.

The $\tilde{\nu}_{\mathrm{EOEM}}$ values can be evaluated, too, to yield $(\mu')^2/a^3$, what can be compared to μ^2/a^3 determined from $\tilde{\nu}_{\mathrm{A,\,max}}$, if induced amounts to μ' are neglected. Table 3 represents these results that have been obtained according to (4) or (5) with 10-CN-ADMA, where $\mu_g = 20 \cdot 10^{-30}\,\mathrm{Cm}$ has been used from [27].

IV. Discussion

It has been shown in Sect. III.2 that a plot of $\tilde{\nu}_{\max}$ versus the solvent parameters g or $g - g'/2$ yields a bent curve instead of a straight line, at least with ADMA, ADEA and 2,6-DM-ADMA. This behaviour may be ascribed to solvent induced, that is reaction field induced changes of the dipole moment of one species. Then consequently polarizability terms must be taken into account. It had been shown in [7] that taking into account such terms, the non-linear plot of $\tilde{\nu}_{\max}$ versus g could be understood consistently with the results from EOEM. The same holds true for the two other molecules where a similar procedure yields a similar procedure yields a similar result. Nevertheless, the large amount of induced moments (larger than the permanent dipole moment, in polar solvents) renders this interpretation somewhat doubtful.

On the other hand, from kinetic investigations comes a lot of evidence that there are at least two species or states that emit the broad fluorescence band. The limiting case would be that of a two state or species model, as discussed in Section III.3. Then, the resulting bent curves of Fig. 6 are to be interpreted a due to the superposition of solvent dependent amounts of an A and a B-fluorescence. The values derived for μ^2/a^3 (Table 1) then are due to the dipole moment μ_{A} of the polar state A emitting the A-fluorescence.

These values for μ^2/a^3 are consistent with assumed dipole moments $\mu_{\mathrm{A}} = 60 \cdot 10^{-30}\,\mathrm{Cm}$ ($\mu = 80 \cdot 10^{-30}\,\mathrm{Cm}$, $\mu_g = 20 \cdot 10^{-30}\,\mathrm{Cm}$, for 10-CN-ADMA), since the values for "a" are in agreement with values estimated from the molecular size of these molecules.

If this latter model were correct, $\tilde{\nu}_{\max}$ of the A-fluorescence, although hidden under the dominant B-fluorescence in non-polar and medium polar solvents can be determined as shown in Section III.3, as $\tilde{\nu}_{\mathrm{EOEM}} \cdot \tilde{\nu}_{\mathrm{EOEM}}$ in non-polar solvents then should be at considerably higher wavenumbers than the observed maximum of the whole fluorescence band, at least with ADMA, ADEA and 2,6-DM-ADMA, as can be predicted by extrapolating the slope of the plots in Fig. 6 in polar solvents, to non-polar ones. Table 2 reveals, that this is not at all the case. As a consequence, the solvatochromic slopes of $\tilde{\nu}_{\mathrm{EOEM}}$ are much smaller than those of $\tilde{\nu}_{\max}$, especially with ADMA, ADEA and 2,6-DM-ADMA. The agreement between the results in Table 1 and 3 for μ^2/a^3 is much better for the other compounds, as are the results for $(\boldsymbol{\mu} - \boldsymbol{\mu}_g)\,\boldsymbol{\mu}/a^3$ for 10-CN-ADMA, which was expected since there is almost no B-fluorescence to be assumed.

Thus these results indicate that the simple two state (species) model is not a sufficient model to describe the behaviour of at least ADMA, ADEA and 2,6-DM-ADMA. These results are in very good agreement with those obtained by Okada et al. [33]. From time dependent transient absorption spectra of ADMA, 2,6-DM-ADMA and MAI in various solvents, they come to the conclusion that the excited state electronic structure of these compounds might change with the solvent polarity, since these spectra cannot be reproduced by a simple two state model. On the contrary, the transient absorption spectra of 3,5-DM-ADMA and TM-ADMA can be reproduced by the superposition of the respective spectra of the locally excited anthracene part (predominant in non-polar solvents) and of the anthracene anion (predominant in polar solvents) which would be in agreement with the TICT model.

Table 1 reveals that the values for μ^2/a^3 of 2,6-DM-ADMA and TM-ADMA determined from solvatochromic slopes of the fluorescence spectrum are significantly larger than those of all other related compounds. Since μ is of the same order as for all other compounds [7, 27, 34], this could be ascribed to the effect of a smaller a^3 of these compounds, which could only be accepted, if the generally assumed proportionality of a^3 and the molecular volume is disregarded.

In another paper [27, 34] dipole moments measured in various solvents by integral electro-optical emission measurements are presented that give further evidence for the different behaviour of these compounds.

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