

## Electronic spectra and structure of nitroanilines

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**Abstract**—Vapour spectra and solution spectra in a variety of solvents were recorded for some  $D, D'-A_r-A$  and  $A, A'-A_r-D$  molecules, where  $D=D'=NH_2$  and  $A=A'=NO_2$ . Ground state dipole moments of  $D, D'-A_r-A$  molecules were determined in dioxane solution.

The molecules in molecules (MIM) molecular orbital method was used to calculate the properties associates with the electronic states. It was found that to the first band in the spectra both charge-transfer and locally excited configurations contribute. The dipole moment in the excited state associated with the first intense electronic transition was evaluated from the solvent shift of the band. A general comparison of theoretical results with experiment reveals a good agreement.

### INTRODUCTION

We have measured the vapour-phase spectra of *o*-*m*- and *p*-nitroaniline and of *m*-dinitrobenzene (Fig. 1). The spectroscopic characteristics of these compounds have been rationalized by GODFREY and MURRELL [1] in terms of locally excited and charge-transfer configurations. In particular it was shown that the inductive effect of the amino and nitro group plays an important role in defining the intensity and position of the transitions with respect to the spectra of the parent compound nitroaniline and nitrobenzene, by lowering the energy of the ring  $\rightarrow$  nitro and amino  $\rightarrow$  ring charge transfer states respectively.

SUPPAN [2] suggests that the measurement of  $\Delta\mu$ , the difference between the excited state  $\mu_e$  and the ground state dipole moment  $\mu_g$  associated with the electronic transition is essential in defining a band as CT. The determination of  $\mu_e$  can be made by the solvent shift method [3].

A comparison between the electronic transitions in the gas-phase with those obtained in cyclohexane solution, reported below, shows that the first band

in nitroanilines undergoes a large bathochromic solvent shift and may be classified as CT band.

The order of the shift in the nitroanilines is  $p > o > m$ , which is the order of the intensity of the band, but is in disagreement with the order of  $\Delta\mu$  values which is  $p > m > o$  [2, 3]. This is a point which needs further investigations, so, whilst a detailed experimental and theoretical study on some mono-substituted nitrobenzenes will be published elsewhere [5], the present work is concerned with the dipole moments in solution and UV spectra in the gas-phase and in a variety of solvents of systems like  $D, D'-A_r-A$  and  $A, A'-A_r-D$ .

In fact it is to be foreseen, on the basis of the above considerations, that the introduction of a donor or an acceptor group in the nitroaniline scheme will make for interesting variations in the ground and excited states electronic structure of the molecule. The "Molecules in Molecules" (MIM) method [6] including the inductive effect of the substituent [7] will be applied in interpreting the electronic properties of the molecules. This method has been successfully used to interpret the electronic spectra of nitro- and amino-nitropyridines [8]. Experimental solvent shift data for *p*-nitroaniline are also reported as reference.

### EXPERIMENTAL

#### Materials

Nitroanilines were commercial products purified by chromatography and crystallization. All solvents were spectrograde.

#### Apparatus and methods

Absorption spectra were carried out with a Unicam SP-1800 spectrophotometer. Vapour phase spectra were

	Band 1	Band 2	Band 3
<i>o</i> -nitroaniline gas	355	260	221
CE	377	269	229
<i>m</i> -nitroaniline gas	326	250 <sub>s</sub>	220
CE	344	270 <sub>s</sub>	235–227
<i>p</i> -nitroaniline gas	292	226	219
CE	322	235 <sub>s</sub>	226
<i>m</i> -nitrobenzene gas	284(weak)	240 <sub>i</sub>	217
CE	296(weak)	—	232
nitrobenzene gas	288(weak)	240	193
NE <sup>4</sup>		252	197

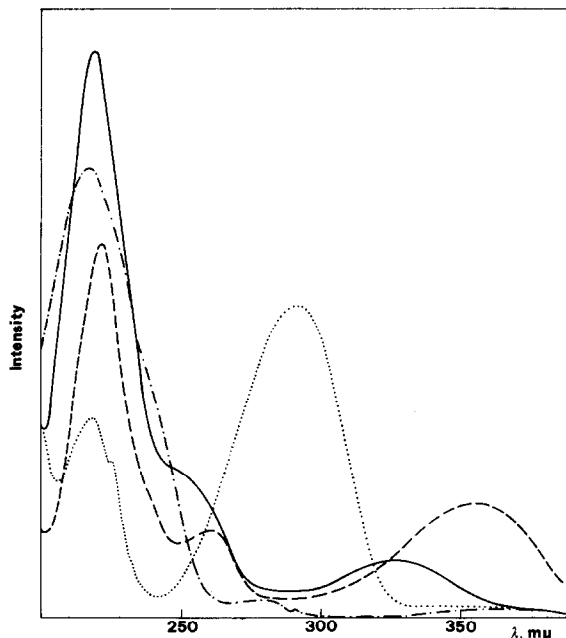


Fig. 1. Vapour spectra of ---- *o*-nitroaniline; — *m*-nitroaniline; ..... *p*-nitroaniline; -.-.-. *m*-dinitrobenzene.

recorded on a Hitachi/Perkin-Elmer model 124 spectrophotometer as previously reported [9]. Dipole moments were determined in dioxane solution at 25+0.1 °C by measuring the dielectric constants with a W.T.W. mod. DM 01 dipolmeter and specific volumes with an Ostwald type pycnometer. The solute molar polarization, extrapolated to infinite dilution, was determined by the Halverstadt-Kumler method [10].

### CALCULATIONS

The  $\pi$ -electronic properties of nitroanilines have been calculated starting from the molecular orbitals localized on benzene, nitro-group and amino-group, which in the formalism of the MIM method are in our case the component fragments. The locally excited states of benzene are shown in Table 1.

For the nitro group the antibonding  $\pi$ -molecular orbital  $\psi_A$  calculated by McEWEN [12]

$$\psi_A = 0.684 \varphi_N - 0.516(\varphi_{O1} + \varphi_{O2})$$

Table 1. Excited states of benzene [11]

State	Wave function	Energy (eV)
$\Lambda_1$	$1/\sqrt{2} (\Lambda_2^4 - \Lambda_1^3)$	4.71
$\Lambda_2$	$1/\sqrt{2} (\Lambda_2^3 + \Lambda_1^4)$	5.95
$\Lambda_3$	$1/\sqrt{2} (\Lambda_2^4 + \Lambda_1^3)$	6.76
$\Lambda_4$	$1/\sqrt{2} (\Lambda_2^3 - \Lambda_1^4)$	6.76

Table 2. Inductive effect of an amino ( $I = +1.74$  eV) and a nitro group ( $I = -1.08$  eV)

Substituent position	$\Delta E$ (eV) of CT configurations				
	$T_D^3$	$T_D^4$	$T_1^A$	$T_2^A$	
NH <sub>2</sub>	1,4	0	+0.58	-0.58	0
	2,3,5,6	+0.44	+0.15	-0.15	+0.44
NO <sub>2</sub>	1,4	0	-0.36	+0.36	0
	2,3,5,6	-0.27	-0.09	+0.09	+0.27

was considered and for the amino group the double occupied  $2p_\pi$  orbital. The energies of charge-transfer configurations, relative to the ground configuration, have been evaluated from the relation:  $E_T = I - A - C + I_\pi c_r^2$  where  $I$  is the  $\pi$ -ionization potential of the donor fragment,  $A$  the  $\pi$ -electron affinity of the acceptor fragment,  $C$  is a coulombic interaction term.  $I_\pi$  is a proportionality factor to account for the inductive effect of substituent and  $c_r^2$  is the  $\pi$ -electron density at the position of the substituent. The following parameters were used in the calculation;

$$I(\text{benzene}) = 9.25 \text{ eV}; \quad A(\text{benzene}) = -1.63 \text{ eV};$$

$$I(\text{NH}_2) = 10.15 \text{ eV}; \quad A(\text{NO}_2) = -0.56 \text{ eV};$$

$$I_\pi(\text{NH}_2) = 1.74 \text{ eV}; \quad I_\pi(\text{NO}_2) = -1.08 \text{ eV}.$$

Energy differences in charge-transfer configurations caused by inductive effects are shown in Table 2. Two-centre electron repulsion integrals ( $\gamma_{\mu\nu}$ ) were evaluated by the PARISER and PARR approximations [13] by the following formulas:

$$(pp/qq)_{C-NH_2} = 13.942 - 4.569r + 0.5020 r^2$$

$$(pp/qq)_{C-O} = 13.200 - 4.205 r + 0.452 r^2$$

$$(pp/qq)_{N-O} = 16.012 - 5.939 r + 0.717 r^2$$

when  $r < 2.80$  Å. For  $r > 2.80$  Å  $\gamma_{\mu\nu}$  have been evaluated from SLATER orbitals.

$(pp/qq)_{N-N}$  values were evaluated by the charged sphere method [14]. An interfragment resonance integral  $\beta$  of  $-1.80$  eV was used [1]. The geometry of the planar compounds was defined by assuming  $R_{C-C} = 1.40$  Å,  $R_{C-NO_2} = R_{C-NH_2} = 1.46$  Å [1];  $R_{N-O} = 1.21$  Å and bond angles  $120^\circ$ .

Single excited configurations for excitation from orbital  $\psi_0$  or to the orbital  $\psi_5$  of benzene were disregarded.

### RESULTS AND DISCUSSION

In Figs. 2 and 3 the gas-phase and solution spectra of nitroanilines are reported. Theoretical

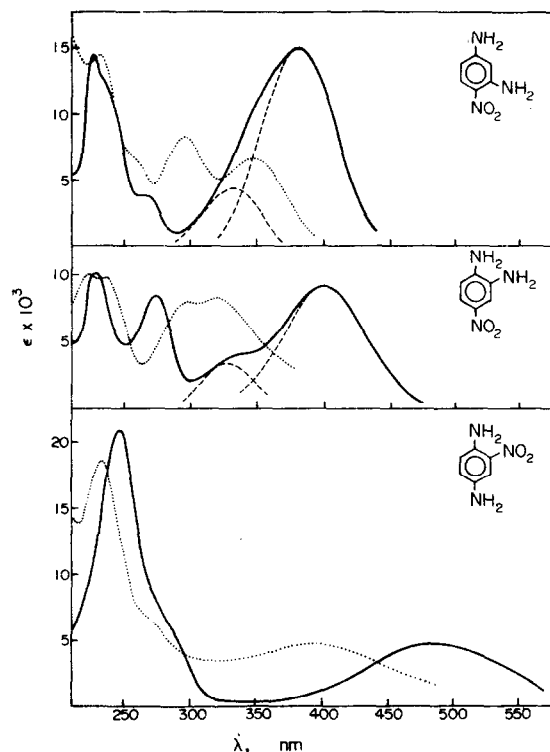


Fig. 2. Vapour spectra .... and solution spectra (acetonitrile) — of D,D'-Ar-A molecules.

results relative to the ground and excited states of nitroanilines are collected in Table 3 and compared with experimental data; mesomeric dipole moments ( $\mu_m$ ) were calculated from the ground and lowest excited states wave functions; a comparison with experimental dipole moments, shown in Table 4, was made by means of a vector compositions of  $\sigma$  group moments and  $\mu_m$  moments. The following  $\sigma$  moments were adopted:  $\mu_\sigma$  C—NO<sub>2</sub> = 3.48 D (the experimental moment of nitromethane);  $\mu_\sigma$  C—NH<sub>2</sub> = 1.15 D at 83.5° with respect to the C—N bond [15];  $\mu_\sigma$  C<sub>A</sub>—H=OD. Inspection of Fig. 2, reveals that in di-donor substituted molecules two bands appear at longer wavelength when a donor group is in *para* position with respect to the acceptor nitro group, while only one band is apparent for the 2,5 substitution (with respect to the nitro group), where the effect of the two donor groups results apparently additive. The separation of the two bands is well accomplished in the vapour spectra while in solution the different medium effect on the electronic transitions tends to their superposition, and from the curve envelope it is possible tentatively to obtain the composition of the bands. The  $\nu_{\text{gas}} - \nu_{\text{CE}}$  shift is of the same order of

magnitude as for the *p*-nitroaniline low-energy band (Figs. 4 and 5). The two bands are therefore CT bands and correspond to the CT bands of the two D—Ar—A systems (compare with the spectra reported in Fig. 1). This result is in accord with the SUPPAN's data relative to the spectra of some di-donor substituted carbonyl compounds [2]. In D,D'-Ar—A molecules the results of calculations in Table 3 show that the charge-transfer configuration  $T_2^A$  and the locally excited configuration  $\Lambda_1$  are the most important contributors to the  $\pi-\pi^*$  transitions. In 2,5-diaminonitrobenzene is  $T_2^A > \Lambda_1$ , which justifies the greater bathochromic shift of the relative  $\pi-\pi^*$  band. The second transition in 2,4- and 3,4-diaminonitrobenzene reveals a higher CT character as  $T_1^A$  configuration than the first one (58 and 48% respectively). In 2,5-diaminonitrobenzene this contribution is smaller (32%) and the band is hidden by the next intense band.

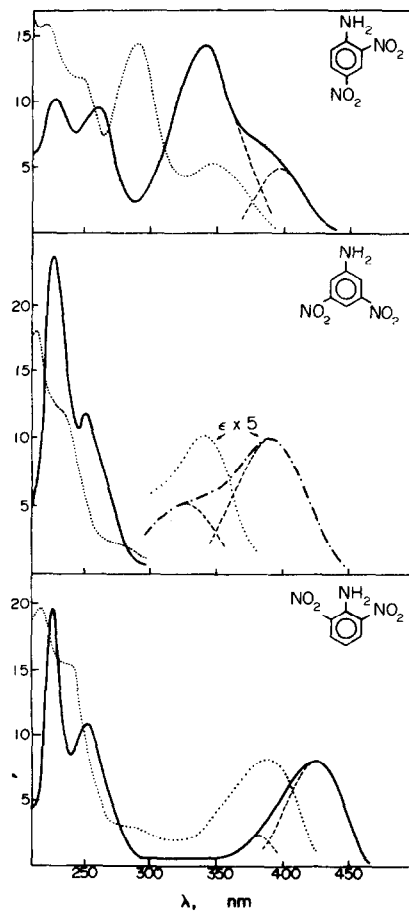


Fig. 3. Vapour spectra .... and solution spectra (acetonitrile) — of A,A'-Ar-D molecules.

Table 3. Electronic states of nitroanilines

State	Energy(eV) <sup>†</sup>		Weight of most important configurations (in%)	Oscillator strength			
	calc.	obs.*		obs.†	calc.	obs.†	$\bar{\mu}_m(D)$
<i>para-nitroaniline</i>							
$\psi_0$	-0.53	—	—	91 $\Gamma$ , 4 $T_D^4$ , 4 $T_1^A$	—	—	1.69
$\psi_1$	4.31	4.24	3.37	81 $\Lambda_1$ , 13 $T_2^A$ , 6 $T_D^3$	0	0.32	2.83
$\psi_2$	4.41						
$\psi_3$	5.41						
$\psi_4$	5.62						
				63 $T_2^A$ , 21 $\Lambda_3$ , 10 $T_D^3$ , 5 $\Lambda_1$	0.34		12.16
				45 $\Lambda_2$ , 34 $T_D^4$ , 17 $T_1^A$	0.18		10.91
					0.06	0.32	7.02
<i>2,4-diaminonitrobenzene</i>							
$\psi_0$	-0.81	—	—	88 $\Gamma$ , 4 $T_1^A$ , 4 $T_D^4$	—	—	1.33
$\psi_1$	3.86	3.58	3.25	35 $\Lambda_1$ , 29 $T_2^A$ , 13 $T_1^A$ , 13 $T_{D_2}^A$	0.06	0.29	7.57
$\psi_2$	4.26	4.22	3.73	58 $T_1^A$ , 20 $\Lambda_1$ , 5 $\Lambda_2$ , 4 $T_{D_4}^A$	0.23		10.34
$\psi_3$	4.82	4.80 s	4.68	32 $\Lambda_1$ , 32 $T_2^A$ , 12 $T_{D_1}^A$ , 8 $\Lambda_3$ , 5 $T_{D_4}^3$	0.09	0.05	7.32
$\psi_4$	5.46	5.40	5.16 s	63 $\Lambda_2$ , 10 $T_{D_4}^4$ , 9 $T_{D_2}^3$ , 6 $T_1^A$	0	—	2.07
$\psi_5$	5.88	—	5.51	35 $\Lambda_4$ , 32 $T_{D_4}^4$ , 17 $T_{D_2}^3$ , 6 $T_1^A$	0.58	0.24	5.40
<i>3,4-diaminonitrobenzene</i>							
$\psi_0$	-0.78	—	—	89 $\Gamma$ , 4 $T_1^A$ , 4 $T_{D_4}^4$	—	—	1.92
$\psi_1$	3.96	3.89	3.10	38 $\Lambda_1$ , 23 $T_2^A$ , 19 $T_1^A$ , 5 $T_{D_3}^4$	0.07	0.18	7.89
$\psi_2$	4.20	4.19	3.79	48 $T_1^A$ , 25 $\Lambda_1$ , 9 $\Lambda_2$ , 5 $T_2^A$ , 4 $T_{D_4}^A$	0.13		9.76
$\psi_3$	4.99	5.30	4.52	51 $T_2^A$ , 23 $\Lambda_1$ , 11 $\Lambda_3$ , 5 $T_{D_4}^3$	0.09	0.15	10.00
$\psi_4$	5.45	5.58	5.44	50 $\Lambda_2$ , 15 $T_1^A$ , 13 $T_{D_4}^4$ , 10 $T_{D_3}^3$ , 5 $T_{D_3}^4$	0.02	0.22	5.84
<i>2,5-diaminonitrobenzene</i>							
$\psi_0$	-0.75	—	—	90 $\Gamma$ , 3 $T_1^A$	—	—	0.58
$\psi_1$	3.47	3.16	2.54	45 $T_2^A$ , 23 $\Lambda_1$ , 10 $T_{D_2}^A$ , 5 $T_{D_5}^A$	0.01	0.09	9.07
$\psi_2$	4.56	4.59 s	4.33 s	45 $\Lambda_1$ , 29 $T_1^A$ , 10 $\Lambda_2$ , 5 $T_{D_2}^A$	0.03	—	5.60
$\psi_3$	4.80						
$\psi_4$	5.22	5.32	5.03	32 $T_2^A$ , 25 $T_1^A$ , 17 $\Lambda_1$ , 12 $\Lambda_2$	0.09		9.19
				26 $\Lambda_2$ , 18 $T_1^A$ , 14 $T_{D_2}^3$ , 11 $\Lambda_3$ , 11 $\Lambda_4$ , 9 $T_{D_3}^3$		0.60	2.61
<i>2,4-dinitroaniline</i>							
$\psi_0$	-0.38	—	—	94 $\Gamma$ , 4 $T_1^A$	—	—	0.70
$\psi_1$	4.31	3.60	3.13 s	75 $\Lambda_1$ , 13 $T_1^A$ , 9 $T_2^A$	0.01	0.30	2.17
$\psi_2$	4.72	4.27	3.66	78 $T_1^A$ , 10 $\Lambda_2$ , 6 $\Lambda_4$	0.33		11.30
$\psi_3$	4.90				0.05		9.88
$\psi_4$	5.43				0.15		7.21
		5.02	4.77	6 $\Lambda_3$		0.18	
$\psi_5$	5.59	5.66	5.44	63 $T_D^A$ , 19 $T_D^4$ , 16 $T_D^3$	0		12.32
$\psi_6$	5.97			48 $T_2^A$ , 21 $\Lambda_1$ , 18 $T_1^A$ , 7 $\Lambda_3$	0.10	0.21	6.49
<i>2,6-dinitroaniline</i>							
$\psi_0$	-0.66	—	—	90 $\Gamma$ , 4 $T_D^4$	—	—	0.25
$\psi_1$	3.64	3.22	2.92	32 $\Lambda_1$ , 20 $T_1^A$ , 20 $T_1^A$ , 10 $T_D^3$	0.001	0.11	0.89
				7 $T_D^A$ , 5 $T_D^A$			
$\psi_2$	4.33	4.35	—	31 $T_1^A$ , 31 $T_1^A$ , 12 $T_D^A$ , 12 $T_D^A$ , 6 $\Lambda_2$	0.004	—	3.42
$\psi_3$	4.77	5.19	4.92	48 $\Lambda_1$ , 11 $T_2^A$ , 11 $T_2^A$ , 9 $T_1^A$ , 9 $T_1^A$	0.01	0.25	2.44
$\psi_4$	5.20						0.26
$\psi_5$	5.62	5.79	5.52	38 $\Lambda_2$ , 32 $T_D^4$ , 15 $\Lambda_4$	0.45	0.23	3.08
$\psi_6$	5.76						32 $T_2^A$ , 32 $T_2^A$ , 10 $\Lambda_1$ , 6 $T_D^A$ , 6 $T_D^A$
<i>3,5-dinitroaniline</i>							
$\psi_0$	-0.64	—	—	91 $\Gamma$ , 4 $T_D^4$	—	—	1.29
$\psi_1$	3.79	3.65	3.17	43 $\Lambda_1$ , 19 $T_1^A$ , 19 $T_1^A$ , 9 $T_D^3$	0	0.04	5.18
$\psi_2$	4.41	4.43 s	3.79 s	30 $T_1^A$ , 30 $T_1^A$ , 16 $\Lambda_2$ , 9 $T_D^4$	0.01	—	7.81
$\psi_3$	4.86	5.16	4.94	35 $\Lambda_1$ , 14 $T_1^A$ , 14 $T_1^A$ , 14 $T_2^A$	0.01	0.24	4.87
$\psi_4$	5.19			14 $T_2^A$			
				27 $\Lambda_2$ , 23 $T_2^A$ , 23 $T_2^A$ , 8 $T_1^A$	0.01		4.94
				8 $T_1^A$			
$\psi_5$	5.81	5.79	5.48	24 $T_2^A$ , 24 $T_2^A$ , 17 $\Lambda_2$ , 12 $T_1^A$	0.01	0.38	7.79
$\psi_6$	5.97			30 $\Lambda_4$ , 21 $T_D^4$ , 17 $\Lambda_2$ , 7 $T_2^A$	0.70		3.25
				7 $T_2^A$ , 6 $T_1^A$ , 6 $T_1^A$			

\* in the vapour phase.

† in acetonitrile solution.

‡  $\bar{\mu}_m$  is the calculated mesomeric moment.

¶ s = shoulder.

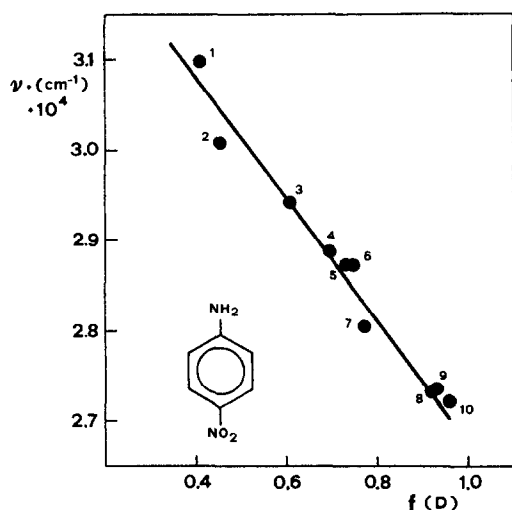


Fig. 4. Plot of  $\nu_a$  against  $f(D)$  for *p*-nitroaniline. Numbers in the plot refer to Table 5.

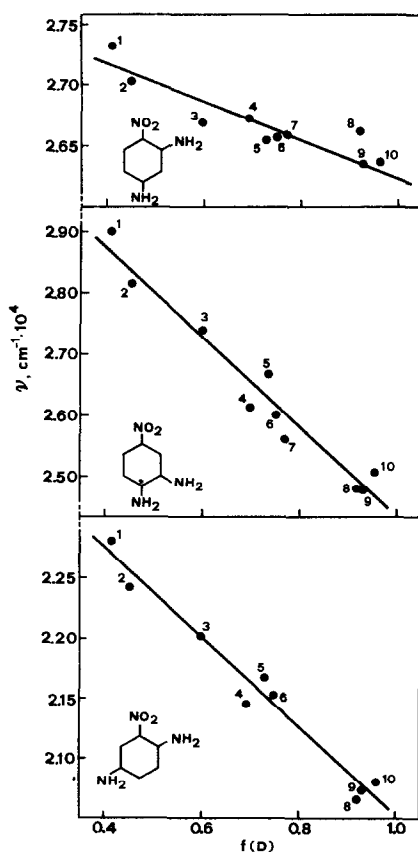


Fig. 5. Plot of  $\nu_a$  against  $f(D)$  for D,D'-A,-A molecules. Numbers in the plot refer to Table 5.

From Fig. 3 it can be seen that in A,A'-Ar-D molecules there are two separate CT bands independently from the position of the substituent. An overall comparison of the theoretical results with experimental data (Table 3) reveals a good agreement both for the transition energies and oscillator strengths. The greatest discrepancy is found for 2,4-dinitroaniline where the theoretical values exceed the experimental transition energies of about 0.7 eV, however the relative position of the bands are correctly predicted in every case. To the first calculated transition the contribution of the locally excited configuration  $\Lambda_1$  ranges from 75% in 2,4-dinitroaniline to 32% in 2,6-dinitroaniline, while the second transition have essentially a CT character ( $T_1^A$  ranges from 78% in 2,4-dinitroaniline to 60% in 3,5-dinitroaniline). The detailed contributions of the various configurations in the other transitions can be seen in Table 3.

The ground state dipole moment found theoretically are compared with the experimental values in Table 4. These are invariably underestimated by about 1 D, however the agreement is to be considered not bad since empirical parameters for the calculations have not been adjusted to obtain the best fit to experiment.

In order to obtain some informations on the charge distribution and dipole moment of the excited states associated with the first intense electronic transition in the examined compounds the solvent-shift method was applied. The selected solvents and their properties are reported in Table 5.

According to McRAE [16] the solvent shift of the electronic transition energy of a polar solute molecule in a series of solvents can be expressed as follows [3]:

$$\Delta E = \Delta\mu_{g-e} \frac{\mu_g}{a^3} \Delta f(D)$$

where  $\mu_g$  and  $\mu_e$  are the dipole moments in the ground and excited states respectively,  $a$  is the radius of the Onsager cavity;  $f(D) = 2(D-1)/(2D+1)$ ;  $D$  = dielectric constant of the solvent. The cavity radius  $a$  was evaluated from the molecular volume as previously described [17]; a mean value of 3,45 Å was obtained. The experimental absorption transition where plotted against  $f(D)$  in Figs. 4, 5 and 6. Fairly straight lines were obtained from which, the  $\mu_e$  values of Table 4 were obtained. Data referring to the *p*-nitroaniline and 3,5-dinitroaniline are in good agreement with those obtained by the more reliable method based on

Table 4. Calculated and experimental dipole moments for ground state and excited state for the first intense band of nitroanilines

Compound	$\mu_g(\text{exp})$	$\mu_g(\text{calc})$	$\Delta\nu/\Delta f(D)$ ( $\text{cm}^{-1}$ )	$\mu_e(\text{exp})^*$	$\mu_e(\text{exp})^\dagger$	$\mu_e(\text{calc})$	$\varphi^\ddagger$
<i>para</i> -nitroaniline	6.29 <sup>§</sup>	5.20	-6439 ± 400	15.23 ± 0.55	15.41	15.55	18.7
2,4-diaminonitrobenzene	7.12 <sup>¶</sup>	5.14	-1488 ± 180	8.94 ± 0.23	9.25	11.13	14.8
3,4-diaminonitrobenzene	7.06 <sup>¶</sup>	5.61	-7230 ± 600	16.00 ± 0.75	16.39	11.40	12.6
2,5-diaminonitrobenzene	5.41 <sup>¶</sup>	4.63	-3661 ± 260	11.32 ± 0.42	11.93	12.75	18.4
2,4-dinitroaniline	5.85 <sup>§</sup>	4.25	-2783 ± 190	10.00 ± 0.29	14.54	13.38	46.5
2,6-dinitroaniline	1.93 <sup>§</sup>	3.55	-1344 ± 260	8.01 ± 1.18	8.11	4.64	9.1
3,5-dinitroaniline	5.45 <sup>§</sup>	4.78	-3117 ± 230	10.45 ± 0.36	10.83	8.61	15.2
			-1892 ± 310	8.48 ± 0.50	8.79		

\* assuming  $\mu_g$  parallel to  $\mu_e$ ;† tacking account of the angle between  $\mu_g$  and  $\mu_e$  as found theoretically.‡ angle defined by  $\mu_g$  and  $\mu_e$  vectors;§ taken from A. L. McCLELLAN, *Tables of Experimental Dipole Moment*. Freeman (1963), in benzene solution.

¶ present work, in dioxane solution.

the electrical dichroism:

$\mu_e(p\text{-nitroaniline}) = 14 \text{ D}$  [18];  $15.5 \pm 2.8 \text{ D}$  [19];

$\mu_e(3,5\text{-dinitroaniline}) = 11.8 \pm 1.1 \text{ D}$  [19].

From Table 4 it can be seen that all the compounds investigated show large values of  $\Delta\mu$  thus confirming the prevailing CT character of the first intense band in the spectrum. A low value is found for 2,4-diaminonitrobenzene, but if we consider the value relative to the second electronic transition located at 4.22 eV in the vapour  $\Delta\mu$  value rises of about 3D; this is probably correct since in the solution spectrum the two bands are superposed and the major contribution to the solvent shift may come from the second band since its greater CT character. The variation of the dipole moment associated to the electronic transition is essentially in the same direction of  $\mu_g$  vector, with exception of 2,4-dinitroaniline for which  $\varphi$  (see Table 4) = 46.5°. There is a good agreement between theoretical and experimental  $\mu_e$  values despite the approximations involved both in the theoretical calculations and in

the solvent shift measurements; the major discrepancy it found in 2,6-dinitroaniline, but in this case, besides the possible steric hindrance to planarity, the presence of strong intra-molecular hydrogen bonding [20] may also be taken into consideration.

Table 5. Properties of solvents

number	solvent	$n_D(25^\circ\text{C})$	$D(25^\circ\text{C})$	$f(D)$
1	cyclohexane	1.42	2.02	0.41
2	carbon tetrachloride	1.46	2.25	0.45
3	trichloro-ethylene	1.48	3.27	0.60
4	diethyl-ether	1.35	4.22	0.68
5	chloroform	1.45	5.14	0.73
6	chlorobenzene	1.52	5.62	0.75
7	ethyl acetate	1.37	6.11	0.77
8	methyl-ethyl-ketone	1.38	18.51	0.92
9	acetone	1.36	20.70	0.93
10	acetonitrile	1.34	36.70	0.96

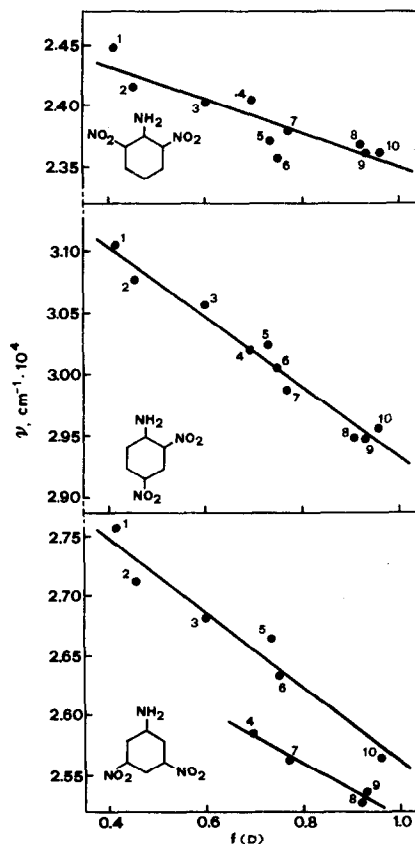


Fig. 6. Plot of  $\nu_a$  against  $f(D)$  for A, A'-A, -D molecules. Numbers in the plot refer to Table 5.

It can be noted that there is no correlation between  $\Delta\mu$  and the intensity, the position and the % CT of the band. Furthermore there is no correlation between  $\Delta\mu$  and the  $\nu_{\text{gas}}-\nu_{\text{CE}}$  shift. These results probably indicate that solvent shift depends essentially on the atomic charge densities both in the ground and excited state of the molecule and that differential solute-solvent interactions are operative for the various compounds of the present series; this may determine the behaviour of 3,5-dinitroaniline (Fig. 6) for which two straight lines can be drawn.

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