Excited State Dipole Moments of Nitrobenzene Derivatives

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The excited state dipole moments of a series of *m*- and *p*-nitrobenzene derivatives of type A–Ph–D have been evaluated from absorption spectra measurements (in the vapour and in solution) by employing various solvent shift equations, and by semiempirical MO methods (MIM and PPP). The μ_e values calculated from different solvent shift equations differ appreciably but they all give the same relative order for the moments and can be used for qualitative comparison of μ_e for a series of closely related compounds. MIM and PPP calculations, in contrast to the experimental findings, give comparable values of μ_e with the same order of magnitude for all the compounds. They also show that generally $\mu_{e(calc)}$ is much greater than $\mu_{e(exp)}$. Results suggest that the excited state dipole moments of the title compounds can be evaluated for qualitative purposes by means of a simplified equation through the measurement of the frequency shift obtained from the gas-phase and solution (apolar solvent) spectra.

KNOWLEDGE of excited state dipole moments (μ_e) is of great importance in the study of the physical–chemical properties of molecules in their excited electronic states.[1-3] The observation of the solvent shift of the electronic absorption and emission spectra is one of the few methods, certainly the simplest, of obtaining experimental information on the excited state dipole moments. Therefore, though the method suffers some limitations for the quantitative evaluation of μ_e,[4] several papers have dealt with solvatochromic effects.[5-9] The complete equations which describe the solvent dependence of the electronic bands are somewhat complex for practical purposes, so that some approximations are generally introduced, and a description of the solvent shift involving only two solvent parameters (*i.e.* the dielectric constant and the refractive index) is generally used.

The aim of this work was to evaluate the excited state dipole moments of a series of *m*- and *p*-nitrobenzene derivatives A–Ph–D (A = acceptor group NO_2; D = donor group of variable donating power) by means of absorption spectra measurements in the vapour and in solution by employing various solvent shift equations in order to compare the μ_e values obtained from each equation with those calculated by semiempirical MO methods and with those obtained by some other more reliable experimental methods in order to evaluate critically the use of the various solvent-shift equations in determining μ_e values.

EXPERIMENTAL

Materials.—Commercially available nitrobenzenes were purified by chromatography and crystallization. All the solvents used were spectrograde.

Apparatus and Methods.—Absorption spectra in solution were carried out with a Unicam SP 1800 spectrophotometer. Gas-phase spectra were recorded with a Hitachi–Perkin-Elmer model 124 spectrophotometer by using an apparatus similar to that described in ref. 10. Solvents used for absorption solvent-shift measurements were selected to give large variations in dielectric constant D and small variations in refractive index n. The selected solvents and their properties are given in Table 1. Solvent-shifts are reported in Table 2.

CALCULATIONS

The Pariser–Parr–Pople (PPP) method with the parametrization suggested by Roos and Skancke [11] and the molecules in molecules (MIM) method [12] were used for evaluating μ_e. For MIM calculations the locally excited states of benzene of ref. 12 are adopted; for the nitro-group the π-MOs calculated by McEwen [13] and for the donor group a doubly occupied $2p_\pi$ orbital were considered. In calculating the energies of charge transfer configurations allowance has been made for the inductive effect of the substituent as reported in ref. 14. The inductive parameters I_π were calculated from the data of ref. 15: $I_\pi(NH_2)$ 1.74; $I_\pi(NO_2)$ −1.08; $I_\pi(OCH_3)$ 1.47; $I_\pi(Cl)$ 0.66 eV. The MIM resonance integrals were calculated by Kon's relationship,[16] all the two-electron two-centre integrals

TABLE 1

Properties of solvents

Solvent	n_D (20°)	D (20°)
n-Hexane	1.375	1.89
Cyclohexane	1.426	2.02
n-Heptane	1.387	1.90
Diethyl ether	1.353	4.33
n-Amyl alcohol	1.411	13.90
Acetonitrile	1.344	37.60

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[1] H. Labhart, *Ber. Bunsengesellschaft Phys. Chem.*, 1976, **80**, 241.

[2] W. Liptay, in 'Excited States', Academic Press, London, 1974, vol. 1, p. 129.

[3] K. M. C. Davis, in 'Molecular Association,' Academic Press, London, 1975, vol. 1, p. 151.

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[5] P. Suppan, *J. Chem. Soc. (A)*, 1968, 3125.

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[11] (*a*) B. Roos and P. N. Skancke, *Acta Chem. Scand.*, 1967, **21**, 233; (*b*) B. Roos, *ibid.*, p. 2318; (*c*) I. Fischer-Hjalmars and M. Sundbom, *ibid.*, 1968, **22**, 607; (*d*) B. Grabe, *ibid.*, p. 2237; (*e*) G. Höjer, *ibid.*, 1969, **23**, 2589; (*f*) O. Gropen and P. N. Skancke, *ibid.*, p. 2685.

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[13] K. L. McEwen, *J. Chem. Phys.*, 1960, **32**, 1801.

[14] S. Millefiori, G. Favini, A. Millefiori, and D. Grasso, *Spectrochemica Acta*, 1977, **33A**, 21.

[15] M. Godfrey and J. N. Murrell, *Proc. Roy. Soc.*, 1964, **A278**, 64.

[16] I. Kon, *Bull. Chem. Soc. Japan*, 1955, **28**, 275.

relative to non-bonded atoms were calculated according to ref. 17. Ionization potentials I, and electron affinities A of each fragment were taken from refs. 18 and 19: NH_2, I 10.15; Cl, I 13.01; OCH_3, I 10.85; CH_3, I 12.99; NO_2, A −0.56; benzene, I 9.25 eV, A −1.63 eV. The geometry of the planar molecules was defined as follows: the benzene ring was assumed to be regular hexagon with R_{C-C} 1.397; R_{C-NO_2} 1.486; R_{N-O} 1.208; R_{C-NH_2} 1.385; R_{C-O} 1.400; and R_{C-Cl} 1.718 Å. The heteroatom model was used for the methyl group following ref. 11.

TABLE 2

Solvent shifts (cm^{-1}) for the first intense electronic transition in nitrobenzene derivatives and % of charge-transfer configurations (in parentheses) as obtained from MIM and PPP calculations respectively

		Substituent							
Solvent	H	*m*-Cl	*m*-NH_2	*m*-CH_3	*m*-OCH_3	*p*-Cl	*p*-NH_2	*p*-CH_3	*p*-OCH_3
n-Hexane		39 800	28 990	38 900	31 450	37 850	31 300	38 100	34 200
n-Heptane	39 730 [a]								
Cyclohexane		39 700	28 820	38 750	31 250	37 800	31 070	37 730	34 030
Diethyl ether		39 150	27 500	38 200	30 800	37 300	28 800	37 050	33 450
Ethyl acetate		38 800	27 200	37 900	30 650	37 100	28 100	36 700	33 000
n-Amyl alcohol		38 800	26 880	37 800	30 650	36 900	26 900		33 000
Acetonitrile		38 600	26 520	37 600	30 400	36 750	27 000	36 150	32 450
Vapour	41 667 [a]	41 300	30 660	40 820	32 920	39 600	34 210	39 850	36 870
	(86—59)	(64—57)	(42—53)	(66—55)	(24—40)	(88—57)	(84—52)	(74—58)	(82—56)

[a] S. Nagakura, M. Kojima, and Y. Maruyama, *J. Mol. Spectroscopy*, 1964, **13**, 174.

TABLE 3

Ground state dipole moments [a] (μ/D) of nitrobenzene derivatives

	MIM						PPP						Experimental
Substituent	μ_σ'	μ_m	μ_{tot}	α [b]	β	γ	μ_σ	μ_π	μ_{tot}	α [b]	β	γ	μ [c]
H	3.48	0.42	3.90	90	0	90	1.15	4.42	5.57	90	0	90	3.93
m-Cl	3.02	0.52	3.30	64.4	25.6	90	1.68	4.46	4.92	70.7	19.3	90	3.40
m-NH_2	3.60	1.24	4.51	103.2	20.0	75.3	1.58	5.57	6.75	104.1	17.3	80.2	4.90
m-CH_3	3.55	0.48	3.98	95.0	5.0	90	1.23	4.75	5.95	93.7	3.7	90	4.25
m-OCH_3 [d] i	2.12	0.71	2.73	100.5	10.5	90	0.22	4.92	4.72	99.7	9.7	90	3.89
ii	4.37	0.71	4.84	81.5	8.5	90	2.21	4.92	6.76	86.5	3.5	90	
p-Cl	1.55	0.75	2.30	90	0	90	0.78	4.42	3.64	90	0	90	2.60
p-NH_2	3.54	1.43	4.91	90	13.4	76.6	1.53	6.36	7.47	90	8.8	81.2	6.29
p-CH_3	3.62	0.59	4.21	90	0	90	1.29	5.07	6.36	90	0	90	4.39
p-OCH_3	3.11	0.91	3.96	72.2	17.8	90	1.32	5.30	5.96	78.3	11.7	90	4.80

[a] For the symbols see text. [b] α, β and γ are the angles which the vector moments makes with the x, y, and z axes, respectively; a left-hand system of axes is taken with the y-axis along the 4–1 direction. [c] A. L. McClellan, 'Tables of Experimental Dipole Moments,' Freeman, San Francisco, 1963. [d] From the *s-cis* (i) and *s-trans* (ii) conformers a mean value of 3.93 and 5.83 D was calculated for the MIM and PPP approximations, respectively, as $\mu = \sqrt{0.5\ (\mu_i^2 + \mu_{ii}^2)}$, to be compared with the experimental value.

Ground state μ_g and excited state dipole moments μ_e were calculated from the ground state and excited state wave function respectively. Experimental and calculated μ_g values are reported in Table 3. In the MIM approximation μ_{tot} was evaluated by the vector composition of μ_σ' and μ_m, where μ_σ' is derived from the vector composition of the group moments of the corresponding aliphatic derivatives, which include electron polarization within the group and μ_m is the calculated interaction moment between the groups; it differs from μ_π in that it represents the polarization which arises from the interaction between polarized fragments. For μ_σ' (C–NO_2) a value of 3.48 D was adopted; other μ_σ' values were taken from ref. 20. In the PPP approximation μ_σ was calculated by the vector composition of bond moments by taking μ_σ (C–N) 0.45 and μ_σ (N–O) 0.30 D, and for other bonds $\mu_\sigma = \mu_\sigma'$.

Inspection of Table 3 shows that PPP calculations reproduce the correct trend of the moment values, but overestimate by *ca.* 1.0—2.0 D the absolute moments. MIM calculations give good agreement between μ_{exp} and μ_{calc} except for *p*-methoxy- and *p*-amino-nitrobenzene where μ_{calc} is 0.8 and 1.3 D, respectively, lower than the experimental value.

Solvent Shift.—The solvent shift equations considered in this work are the Lippert[21] equation (1) where $f(D) = 2(D - 1)/(2D + 1)$ and $f(n^2) = 2(n^2 - 1)/(2n^2 + 1)$ which on

$$-\Delta E = \frac{(\mu_e - \mu_g)\mu_g}{r^3}\Delta[f(D) - f(n^2)] + \frac{\mu_e^2 - \mu_g^2}{r^3}\Delta f(n^2) \quad (1)$$

the assumption of equal refractive index for all solvents becomes (2) and equations (3) and (4), recently proposed by

$$-\Delta E = \frac{(\mu_e - \mu_g)\,\mu_g}{r^3}\Delta f(D) \quad (2)$$

Amos and Burrows,[8] where $\Phi(D) = (D - 1)/(D + 2)$ and $\Phi(n^2) = (n^2 - 1)/(n^2 + 2)$.

Equations (4) and (3) are considered valid if solvent–

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[17] G. Favini and F. Zuccarello, *Gazzetta*, 1960, **99**, 300.

[18] M. Godfrey and J. N. Murrell, *Proc. Roy. Soc.*, 1964, **A278**, 71.

[19] V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvev, and Ye L. Frankevich, 'Bond Energies, Ionization Potentials and Electron Affinities,' Edward Arnold, London, 1966.

[20] A. Millefiori, G. Favini, and S. Millefiori, *Z. Phys., Chem. Neue Folge*, 1975, **94**, 167.

[21] E. Lippert, *Ber. Bunsengesellschaft Phys. Chem.*, 1957, **61**, 562.

dipole reorientation on excitation does or does not occur, respectively.

$$-\Delta E = \frac{2}{r^3}(\mu_e - \mu_g)\mu_g\Delta[\Phi(D) - \Phi(n^2)] + \frac{\mu_e^2 - \mu_g^2}{r^3}\Delta\Phi(n^2) \tag{3}$$

$$-\Delta E = \frac{\mu_e^2 - \mu_g^2}{r^3}\Delta[2\Phi(D) - \Phi(n^2)] \tag{4}$$

Because equations (1) and (3) are not easy to use, Amos and Burrows[8] introduce the approximation $\mu_e^2 - \mu_g^2 = 2\,\mu_g(\mu_e - \mu_g)$ to give (5) and (6).

$$-\Delta E = \frac{(\mu_e - \mu_g)\mu_g}{r^3}\Delta\,[\mathrm{f}(D) + \mathrm{f}(n^2)] \tag{5}$$

$$-\Delta E = \frac{2(\mu_e - \mu_g)\mu_g}{r^3}\Delta\Phi(D) \tag{6}$$

$$-\Delta E = \frac{\mu_e^2 - \mu_g^2}{r^3}\Delta f(D) \tag{7}$$

Moreover equation (1) becomes (7)[8] when the dipole reorientation effect is considered. All these equations neglect changes in the solute polarizability upon excitation. Equation (6) can also be obtained from (3) on the assumption of equal refractive index for all solvents.

TABLE 4

Coefficients of solvent shift equation in nitrobenzene derivatives

		Substituent							
Equation*	H	*m*-Cl	*m*-NH$_2$	*m*-CH$_3$	*m*-OCH$_3$	*p*-Cl	*p*-NH$_2$	*p*-CH$_3$	*p*-OCH$_3$
(2), (7) *a*		40 518 ± 126	30 481 ± 99	39 648 ± 90	31 951 ± 124	38 474 ± 56	34 192 ± 286	39 137 ± 159	35 169 ± 211
b		−2 017 ± 175	−4 147 ± 129	−2 135 ± 125	−15 90 ± 172	−17 70 ± 78	−7 813 ± 399	−3 112 ± 235	−2 658 ± 294
(4) *a*		39 900 ± 111	29 214 ± 170	38 997 ± 91	31 464 ± 99	37 939 ± 51	31 801 ± 342	38 186 ± 144	34 372 ± 123
b		−849 ± 107	−1 751 ± 164	−902 ± 88	−669 ± 96	−754 ± 49	−3 294 ± 331	−1 307 ± 152	−1 140 ± 119
(5) *a*		41 333 ± 238	32 151 ± 361	40 517 ± 180	32 589 ± 230	39 203 ± 90	37 427 ± 373	40 536 ± 131	36 232 ± 295
b		−2 071 ± 221	−4 254 ± 334	−2 198 ± 167	−1 628 ± 213	−1 830 ± 84	−8 094 ± 346	−3 354 ± 127	−2 720 ± 366
(6) *a*		40 107 ± 137	29 640 ± 214	39 218 ± 112	31 626 ± 126	38 125 ± 57	32 985 ± 145	38 517 ± 167	34 649 ± 157
b		−1 718 ± 221	−3 539 ± 346	−1 826 ± 180	−1 352 ± 199	−1 528 ± 92	−7 665 ± 269	−2 679 ± 292	−2 303 ± 253
(8) *c*	−5 077	−3 919	−4 506	−5 070	−4 090	−4 409	−7 690	−5 192	−6 956
(9) *c*	−8 218	−6 238	−7 173	−8 070	−6 511	−7 018	−12 242	−8 265	−1 1072

* For equations see text; *a* and *b* are the intercept (cm^{-1}) and slope (cm^{-1}) of the equation respectively; *c* is the slope (cm^{-1}) of the line drawn between the vapour and cyclohexane (n-heptane for nitrobenzene).

TABLE 5

Dipole moment changes (μ/D) for the first intense π–π^* transition in nitrobenzene derivatives

		Equation							Theoretical	
Substituent	r/Å	(2)	(4)	(5)	(6)	(7)	(8)	(9)	PPP	MIM
H	3.20		0.93 *	4.27 *	2.05 *	1.78	3.03	4.37	9.21	12.51
m-Cl	3.34	4.39 ± 0.38	0.88 ± 0.11	4.51 ± 0.48	1.87 ± 0.24	1.75 ± 0.19	2.99	4.25	8.69	8.75
m-NH$_2$	3.35	6.32 ± 0.20	1.19 ± 0.12	6.49 ± 0.51	2.70 ± 0.26	2.52 ± 0.10	2.71	3.96	9.70	4.48
m-CH$_3$	3.37	3.82 ± 0.22	0.74 ± 0.07	3.93 ± 0.30	1.63 ± 0.16	1.61 ± 0.11	3.29	4.73	8.98	9.45
m-OCH$_3$	3.43	3.28 ± 0.35	0.64 ± 0.10	3.36 ± 0.44	1.39 ± 0.20	1.39 ± 0.17	3.05	4.37	6.63	2.73
p-Cl	3.37	5.18 ± 0.23	0.93 ± 0.07	5.35 ± 0.25	2.23 ± 0.13	1.90 ± 0.11	3.77	5.22	9.63	12.77
p-NH$_2$	3.45	10.13 ± 0.52	1.86 ± 0.21	10.50 ± 0.45	4.97 ± 0.17	3.87 ± 0.25	3.85	5.70	11.68	11.89
p-CH$_3$	3.37	5.39 ± 0.41	1.01 ± 0.13	5.81 ± 0.22	2.32 ± 0.25	2.16 ± 0.20	3.29	4.73	9.76	10.63
p-OCH$_3$	3.41	4.36 ± 0.48	0.86 ± 0.10	4.46 ± 0.60	1.89 ± 0.21	1.83 ± 0.24	4.04	5.78	10.35	11.14

* Ref. 26.

RESULTS AND DISCUSSION

When the above equations are applied to the solvent-shift data of Table 2, the results reported in Tables 4 and 5 are obtained. The radius of the cavity r was evaluated as previously reported.[22] It can be seen that the μ_e values calculated from the different equations differ noticeably. However, they all give the same relative order of moments and thus can at least be used for qualitative comparison of μ_e values in a series of closely related compounds or to compare $\Delta\mu$ shifts within a single compound associated with various electronic transitions.

To check the validity of the equations in determining the correct solvent shifts and the absolute value of μ_e we can compare the experimental ν_{gas} values with those obtained from the parameters of the equations and the present μ_e values with those obtained from more reliable experimental methods. Equations (2) and (7) reproduce to a good approximation ν_{gas} values of *m*- and *p*-amino derivatives; equation (5) gives approximate values of ν_{gas} for some compounds but noticeably overestimates ν_{gas} for *m*- and *p*-amino derivatives; all other equations underestimate ν_{gas} values in all cases. To refer the solvent shift to ν_{gas} we chose a single reference apolar solvent, cyclohexane. The method requires careful determination of two frequencies. In this way equations (1), (3), and (4) were simplified to give (8) and (9), respectively, since for cyclohexane $\mathrm{f}(D) \cong \mathrm{f}(n^2)$ and $\Phi(D) \cong \Phi(n^2)$. Results are reported in Tables 4 and 5.

$$-\Delta E = \frac{\mu_e^2 - \mu_g^2}{r^3}\Delta \mathrm{f}(n^2) \tag{8}$$

$$-\Delta E = \frac{\mu_e^2 - \mu_g^2}{r^3}\Delta\Phi(n^2) \cong \frac{\mu_e^2 - \mu_g^2}{r^3}\Delta\Phi(D) \tag{9}$$

Concerning μ_e values a comparison between our results and those from other more reliable methods is limited to nitrobenzene and *para*-nitroaniline for which data based on the electrochromic effect are available: μ_e (*para*-nitroaniline) 14,[2,23] 15.5 ± 2.8,[24] 12 D;[2]

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[22] G. Favini, A. Gamba, D. Grasso, and S. Millefiori, *Trans. Faraday Soc.*, 1971, **67**, 3139.

[23] J. Czekalla and G. Wick, *Z. Electrochem.*, 1961, **65**, 727.

[24] W. Liptay, W. Eberlein, H. Weidenberg, and O. Elflein, *Ber. Bunsengesellschaft Phys. Chem.*, 1967, **71**, 548.

μ_e(nitrobenzene) 3.5,[2] 9 D.[25] It can be seen that only Lippert's equation (2) and Amos and Burrow's equation (5) give fair agreement with the μ_e values of refs. 2, 23, and 24. Equation (9) shows good agreement with μ_e values of refs. 2 and 24 for *para*-nitroaniline and with the μ_e value of ref. 25 for nitrobenzene. Therefore, it appears that equation (9), in the absence of a wider experimental examination, can be used for the experimental determination of μ_e, though with some caution. The present experimental μ_e values of nitrobenzene derivatives are compared with the corresponding theoretical values obtained by the MIM and PPP methods (Table 5). The two methods give comparable values of μ_e. Furthermore the dominant contributions to the electronic transition considered are of charge-transfer type T_B^A and are almost of the same order of magnitude for all the compounds (Table 2) with the exception of *m*-nitroaniline and *m*-nitroanisole, where the dominant contribution to the electronic transition is, especially in the MIM approximation, of the locally excited benzene type. Indeed small contributions of highly polar charge transfer states of type T_D^A are present in the excited state of the *para*-derivatives. Thus, if $\Delta\mu$ values can be referred to the charge-transfer character of the transition, it is expected that (i) there should not be very large $\Delta\mu$ differences in the series of compounds with the exception of *m*-nitroaniline and *m*-nitroanisole, for which rather low values are expected, owing to the different nature of the transition and (ii) *para*-derivatives should display somewhat higher Δ_μ values than *meta*-derivatives. Data reported in Table 5, columns 10 and 11, show this trend.

The above theoretical predictions are in general agreement with the experimental results of equations (8) and (9). This may be considered as further support for the applicability of these equations for qualitative evaluation of μ_e.

On the other hand, other solvent-shift equations show that Δ_μ values are rather spread out and that the nature of the substituent is more important than the relative orientation of the substituents in determining the relative order of the compounds. A possible explanation of this behaviour is that in polar solvents some specific interactions (*i.e.* hydrogen bonds, charge-transfer interactions) may be present and could be more dependent on the nature of the substituent (*i.e.* on bond polarity and polarizability) than on its orientation. Comparison between $\mu_{e(\mathrm{calc})}$ and $\mu_{e(\exp)}$ reveals that $\mu_{e(\mathrm{calc})}$ is generally much greater than $\mu_{e(\exp)}$; for *p*-nitroaniline only $\mu_{e(\mathrm{calc})}$ is in fair agreement with $\mu_{(\exp)}$ obtained by equations (2) and (5).

To investigate this point further, the electron affinity of the nitro group was varied in order to see the effect of this parameter on the calculated (MIM) values of $\Delta\mu$. Electron affinity values of the nitro group of -0.4 and -0.7 eV were used. For nitrobenzene we obtained Δ_μ 12.78 and 12.19 D, respectively; for *p*-nitroaniline 12.51 and 11.37 D, respectively. These results show that although $\Delta\mu$ increases with increasing electron affinity, as expected, the difference between $\mu_{(\exp)}$ and $\mu_{(\mathrm{calc})}$ is not attributable simply to an inadequate value of the electron affinity.

While it is known that the PPP method somewhat overestimates the contributions of polar forms, the MIM method probably requires a reparametrization to describe excited states adequately. However the difference $\Delta\mu_{(\exp)} - \Delta\mu_{(\mathrm{calc})}$ is also probably affected by an underestimation of $\mu_{(\exp)}$, whose value is particularly sensitive to the size of the cavity radius which is known only approximately.

Conclusions.—From the experimental and theoretical results it seems that the vapour to non-polar solvent effect may be considered the most appropriate method to determine, at least qualitatively, $\Delta\mu$ values through equation (9); equation (8) uses the f(*D*) function and is less accurate. Lippert's equation (2) gives some good results in that it reproduces the ν_{gas} values of *m*- and *p*-nitroaniline and the μ_e values of refs. 2, 23, and 24, and it can be used for the determination of μ_e in the absence of experimental ν_{gas} values. Equations (4) and (7) give incorrect results so that solvent–dipole reorientation does not occur in the nitrobenzene derivatives. Unreliable results from equations (5) and (6) probably derive from the approximation $\mu_e^2 - \mu_g^2 = 2\ \mu_g(\mu_e - \mu_g)$, which is particularly drastic when $\Delta\mu \geqslant 1$,[26] as in the present case.

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