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Studies of azo–hydrazone tautomerism and H-bonding in azo-functionalized dendrimers and model compounds

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This paper is dedicated to Professor Otto Exner in recognition of his outstanding contributions to physical organic chemistry and chemometrics.

Abstract

A ^{13}C NMR and UV–visible study of the tautomeric behaviour of azo-functionalized PAMAM (polyamidoamine) dendrimers and the corresponding model compounds in a variety of solvents is reported. Results of these studies indicate that the azo-functionalized PAMAM dendrimers exist as an equilibrium mixture of azo and hydrazone tautomers. A comparison of the behaviour of the dendnmers with model compounds suggests that the dendrimer periphery affects the tautomeric equilibrium between the azo and the hydrazone forms. The results further show that the proportion of the azo tautomer increases with dendrimer generation as well as in the presence of hydrogen-bond donor solvents such as acetic acid and 2,2,2-trifluoroethanol. Results of MO calculations suggest that the more planar azo tautomer would be favored because it stacks better on the dendrimer surface, which is consistent with experimental results. © 2002 Published by Elsevier Science Ltd.

Keywords: Dendrimers; Azo compounds; Hydrazones; Tautomerism; Hydrogen bonding

1. Introduction

Azo colourants containing hydroxy and amino substituents *ortho* or *para* to the azo groups can in principle exist as mixtures of azo and hydrazone tautomers. While azo–hydrazone tautomerism is quite interesting from a theoretical viewpoint, it is also important from a practical standpoint because the two tautomers have different technical properties [1].

Although quantitative evaluation of the tautomeric equilibria associated with arylazonaphthol dyes has been conducted in the past using UV–visible [2] and NMR [3] spectroscopy, these methods have key limitations. In the case of UV–visible spectroscopy, the equilibrium constant (K_T) cannot generally be obtained directly because the molar extinction coefficient of the individual tautomers cannot be determined, due to the overlapping peaks of the two forms. To overcome this difficulty, semi-quantitative approaches using various assumptions and approximations have been used to quantify the tautomeric equilibrium [4,5]. In the case of NMR spectroscopy, the equilibrium between

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the azo and hydrazone tautomers is rapidly established on the NMR time scale (lifetime of tautomers ~0.2 ms) [6], which renders ^{1}H NMR unsuitable for establishing the position of the tautomeric equilibrium. However, ^{15}N [7,8], ^{14}N [6], and ^{13}C [9] NMR chemical shift data can readily be employed to study quantitatively the tautomenc equilibrium.

As part of investigations of monoazo pigment-functionalized Starburst polyamidoamine (PAMAM) dendrimers based on phenylazo, naphthalimide azo and phthalimide azo derivatives [10], we report herein a quantitative study of the tautomeric behaviour of model azo dyes containing a 2-naphthol-3-anilide moiety and the corresponding azo-modified PAMAM dendrimers (cf. Fig. 1). The results of these studies provide the basis for describing the effect of the dendrimer periphery on the tautomerism of the pendant azo dyes.

While arylazonaphthol dyes generally exist as mixtures of azo and hydrazone tautomers [11], in some cases they exist predominantly in the hydrazone form [12]. Tautomerism in the present dyes can be illustrated using the model compound **2**, which can exist as the azo (**2A**) and hydrazone (**2H**) forms (Fig. 2). Intramolecular H-bonding can occur in both forms. However, for this anilide

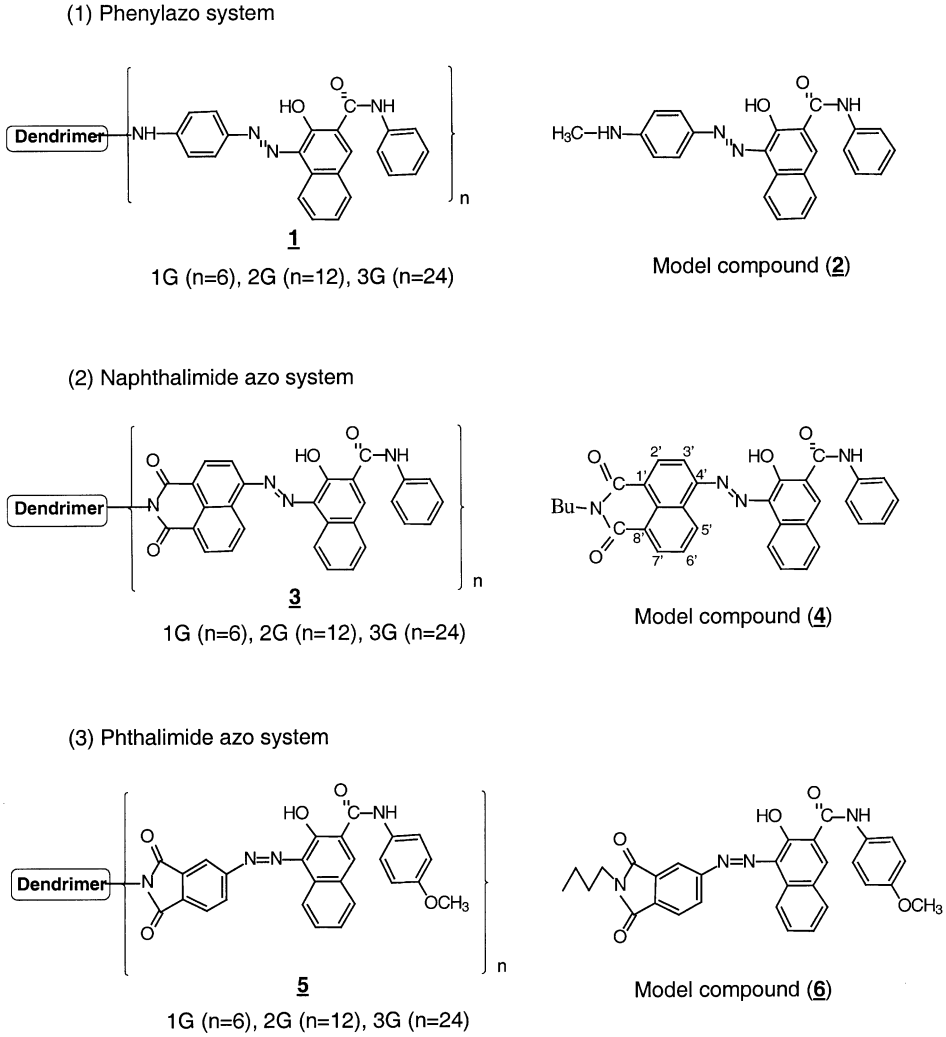


Fig. 1. Structures of azo-functionalized PAMAM dendrimers and corresponding model compounds investigated.

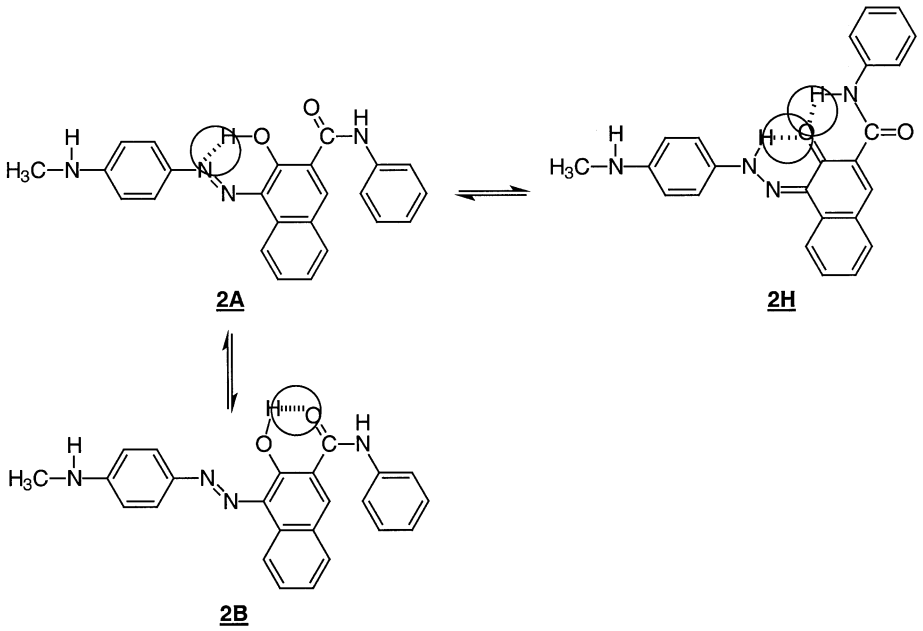


Fig. 2. Illustrations of azo–hydrazone tautomerism and hydrogen bonding in dye **2**.

derivative the hydrazone tautomer can have a bifurcated hydrogen bond, while in the azo form, hydrogen bonding can occur between the OH group and the azo nitrogen (cf. **2A**) or the carbonyl oxygen (cf. **2B**). Results of previous studies have shown the hydrazone form to be favoured in azo dyes containing the 2-naphthol-3-anilide moiety [13–15].

2. Experimental

Full details of the synthesis and characterization of dendrimers and model compounds will be reported elsewhere [10]. ^{13}C NMR spectra were obtained using a Bruker AM400 ($^{13}C = 100.6$ MHz) or a Bruker AC-F 200 spectrometer ($^{13}C =$ 50.3 MHz), normally in $CDC1_3$ and DMSO-d_6. Chemical shifts are reported in parts per million (ppm) relative to $CHCl_3$ ($\delta = 77$ ppm) and DMSO ($\delta = 49$ ppm). UV–visible absorption spectra were obtained using a Hewlett-Packard HP8452A diode array spectrophotometer fitted with a thermostated cell compartment. For UV–visible studies, DMSO and EtOH were purified by distillation from calcium hydride and magnesium, respectively. Other organic solvents used in this study were *N,N*-dimethylformamide (DMF), 2,2,2-trifluoroethanol (TEE), acetonitrile, toluene, chloroform, 1,4-dioxane, acetone, methanol, and hexane. All were of spectroscopic grade and were purified, when necessary, according to accepted procedures.

Stock solutions (0.1–1 mmol) of the dendrimer compounds were prepared by accurately weighing 1–10 mg of compound and dissolving it in 1–5 ml of DMF or DMSO in volumetric flasks that were wrapped in aluminium foil to prevent possible light-induced structural changes. Stock solutions (1–10 mmol) of the model compounds were prepared in $CHCl_3$ or DMF and were stored in the refrigerator. All UV–visible spectra were obtained by injecting 20–50 μl of the stock solution into a 10-mm cuvette containing 2.5 ml of the solvent, shaking the cuvette a few times, and allowing any air bubbles to escape before taking the spectrum.

3. Results and discussion

3.1. Evidence of tautomerism

Using ^{13}C NMR spectroscopy, the C-2 chemical shifts (in $CDCl_3$) of model compounds

2, **4**, and **6** were compared with the corresponding chemical shift for the coupler molecule naphthol AS (cf. Fig. 3). It is clear that the chemical shifts for C-2 in the model compounds are much further downfield than the C-2 signal for naphthol AS. In the case of dye **2**, C-2 is less deshielded due to the presence of the electron-donating amino substituent. If the azo tautomer were to exist exclusively, the C-2 chemical shifts for the model compounds should be in the 160–165 ppm range, once the deshielding effect of the azo moiety is taken into account.

The C-2 chemical shifts for compounds **4** (179.53) and **6** (178.42) are observed in the range expected for carbonyl carbons [16,17]. This downfield shift for C-2 was also observed in the corresponding dendrimers (**3** and **5**), indicating that the hydrazone tautomer predominates in solution.

UV–visible absorption spectra were recorded on the dendrimer and model compounds in various solvents. Representative spectra for model compound **2**, which has the phenylazo structure, are illustrated in Fig. 4. The spectral changes clearly reflect higher proportions of the hydrazone tautomer in the less polar solvents. Interestingly, it was found that the tautomeric behaviour of model compound **4** is slightly different from that of the dendrimers (Fig. 5). It is apparent that the tautomeric equilibrium in this model compound does not change significantly upon varying the solvent. For dendrimer **3**, however, the proportion of azo tautomer increases in solvents with hydrogen bond donor properties, e.g acetic acid and TFE.

Isosbestic points are observed at 548 nm for the phenylazo system (Fig. 4) and at 530 nm for the naphthalimide azo system (Fig. 5). Though not sharp, due to solvent effects, the existence of isosbestic points is consistent with the presence of two components, i.e. azo and hydrazone tautomers.

3.2. Quantitative studies of tautomerism

3.2.1. ^{13}C NMR studies

Although the NMR spectra (or chemical shifts data) for the individual tautomers cannot be obtained, due to the rapid tautomeric equilibrium, the ratio of azo to hydrazone tautomers can be approximated through comparison with the ^{13}C chemical shifts of the model compounds. For example, dye **7** (Fig. 6) exists only in the hydrazone form [9], compound **8** only in the azo form [9], and compound **9** as a mixture of two tautomers. The chemical shifts of C-1′–C-4′ (especially C-1′) in **7** and **8** can be used to establish the tautomeric ratio for dye **9**. The C-1′ chemical shift values in DMSO-d_6 are 140.9 ppm [9] for **7** (hydrazone), 152.3 ppm [9] for **8** (azo) and 144.8 ppm for **9** (mixture). If the C-1′ chemical shift value for 100% hydrazone form is taken as 140.9 and that for 100% azo form as 152.3 ppm, then the percentage of azo form in **9** can be estimated as 34%.

In the present case, only the phenylazo systems (dendrimer **1** and model compound **2**) are suitable for estimating the tautomeric ratio by comparison with the chemical shifts of **7** and **8**, since only these systems are structurally similar to **7** and **8**. The pertinent ^{13}C chemical shifts data for phenylazo compound **2** and dendrimer **1**, as well compounds **7**, **8** and **9** are summarized in Table 1.

Assignment of the C-1′ chemical shifts of model compound **2** and dendrimer **1** can be achieved by applying differential correction factors that are calculated from ^{13}C NMR data for *N*-methylaniline [18] and benzene [19] in DMSO, since ^{13}C chemical shifts generally follow an additivity rule reasonably well [20]. The substituent chemical shifts for C-1′–C-4′ are −11.6, −0.1, −16.0 and 21.9, respectively. Using these values, one can remove the substituent effect and calculate ^{13}C chemical shifts for the phenyl group carbons in model compound **2** and dendrimer **1**. In this regard, we obtained 145.9 (C-1′), 122.5 (C-2′), 128.3 (C-3′), and 130.1 (C-4′) for **2** and 149.7 (C-1′), 122.5 (C-2′), 128.4 (C-3′), and 130.1 (C-4′) for **1**. Based on a comparison of the C-1′ chemical shifts for **1** and **2** with those in model compounds **7** and **8** one can estimate the percentage of azo tautomer for model compound **2** and dendrimer **1** to be 43% for **2** and 76% for **1**. The increase in the percentage of azo tautomer for model compound **2** (43%) compared with **9** (34%) arises from the ability of the electron-donating amino group in compound **2** to better stabilize the azo tautomer. This stabilization will be less effective in the hydrazone form, due to

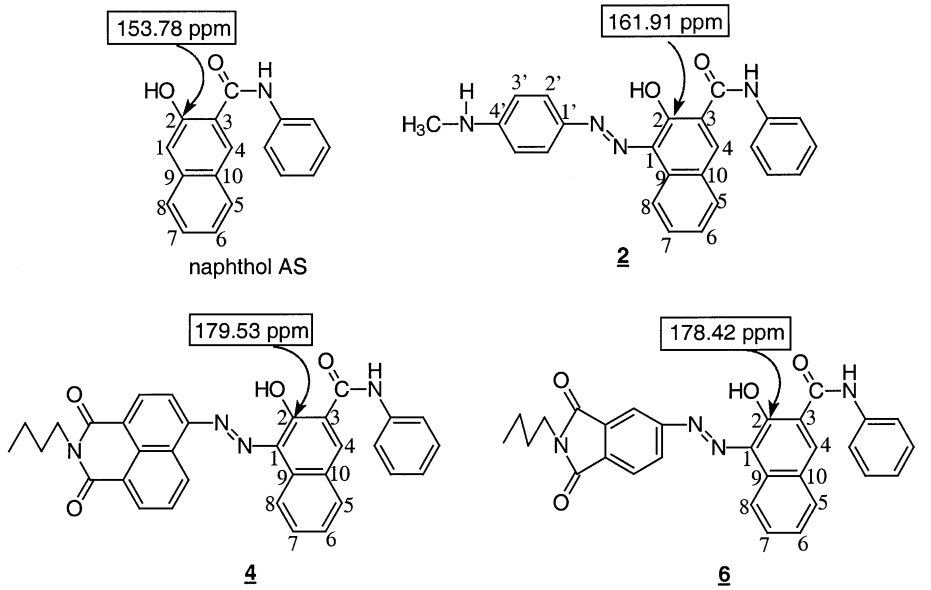


Fig. 3. ^{13}C NMR chemical shifts in compounds **2**, **4**, **6** and in naphthol AS coupler.

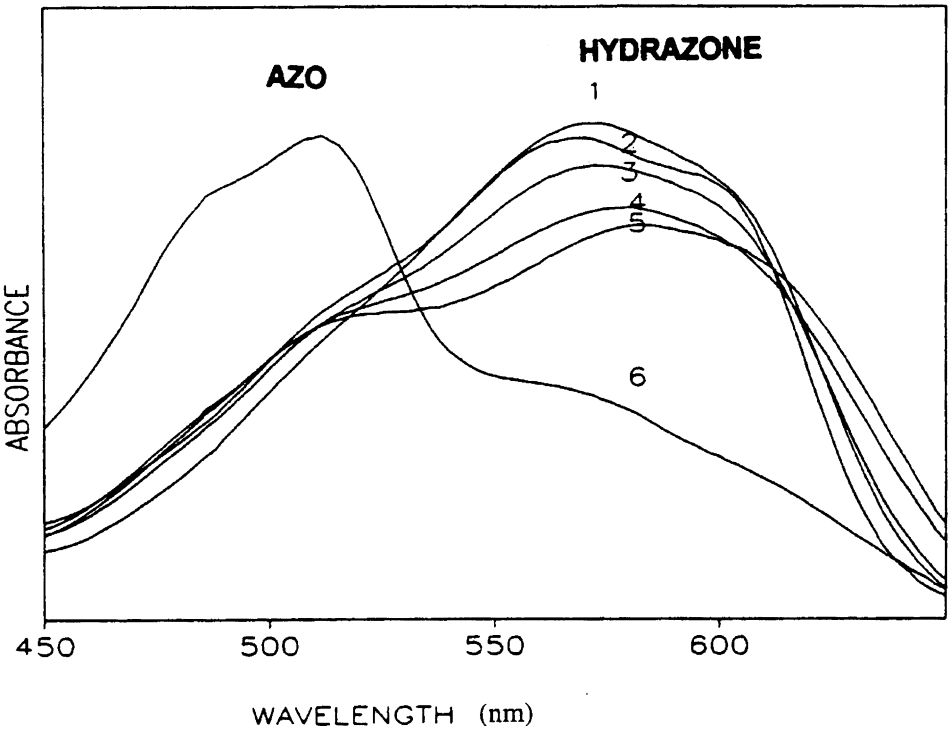


Fig. 4. UV–visible spectra of model compound **2** in chloroform (1), toluene (2), 1,4-dioxane (3), acetonitrile (4), acetone (5), and TFE (6).

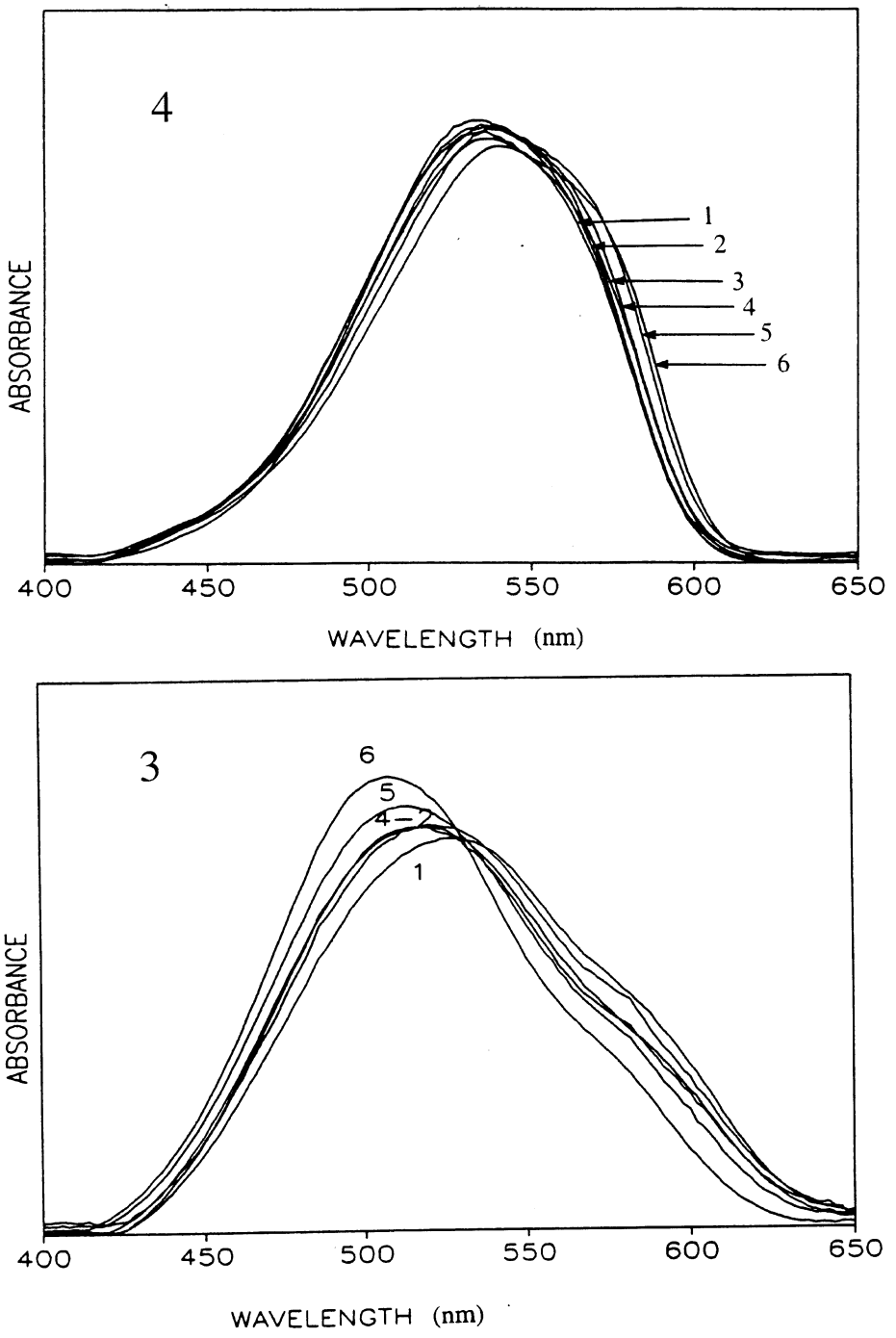


Fig. 5. Comparison of UV–visible spectra of model compound **4** and the naphthalimide azofunctionalized dendrimer **3** in toluene (1), acetone (2), acetonitnle (3), ethanol (4), methanol (5), and TFE (6).

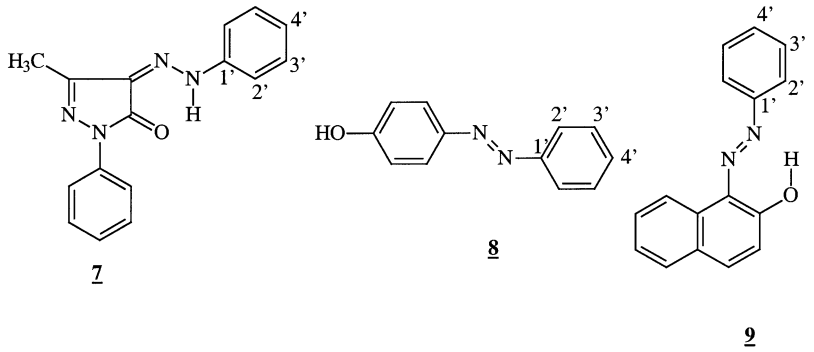


Fig. 6. Azo compounds existing in hydrazone form (**7**), azo form (**8**), and as mixture of the two tautomers (**9**).

the electron-donor properties of the imino linkage (–NH–N=) in this tautomer. It is interesting that the percentage of azo tautomer in dendrimer **1** increases to 76% compared with 43% in model compound **2**, which clearly indicates that the dendrimer periphery plays an important role in the tautomeric equilibrium.

Although it is reasonable to assume that C-1′ is more sensitive than the other C-atoms to electronic effects arising from changes in the azo-hydrazone tautomeric equilibrium, it could be argued that the use of the C-2′ and C-4′ chemical shifts in tandem would strengthen the reliability of our estimation of the tautomer composition. As noted earlier, for compounds **1** and **2**, the corrected ^{13}C chemical shifts for C-2′ (122.5) and C-4′ (130.1) are quite similar to those in model azo compound **8** (C-2′ = 122.3 and C-4′ = 130.1). This would suggest that compounds **1** and **2** exist almost exclusively in the azo form, an unlikely result for an arylazonaphthol dye containing the 2-naphthol-3-anilide moiety. At present, the discrepancy in the azo content in **1** and **2** that was calculated from chemical shift comparisons involving C-1′, versus C-2′ and C-4′, is not readily explainable.

Table 1
^{13}C NMR chemical shifts data for C-1′–C-4′ and the % azo tautomer for dyes **1**, **2**, **7**, **8** and **9**

Compounds	^{13}C chemical shifts (in ppm)[a]				% Azo form
	Cl′	C2′	C3′	C4′	
7	140.9	115.6	129.5	125.6	0
8	152.3	122.3	129.5	130.1	100
9	144.8	118.3	129.5	127.1	34
Model (**2**)	134.3	122.4	112.3	152.0	43
Dendrimer (**1**)	138.1	121.5	112.4	150.4	76

[a] ^{13}C NMR data were obtained in DMSO-d_6.

While the approach of comparing ^{13}C NMR chemical shifts has provided an approximate ratio of azo tautomer in the phenylazo system, some limitations need to be pointed out for application in the present system. First, studying tautomerism in a variety of solvents cannot be readily achieved because of the requirement of a concentration $\geqslant 10^{-3}$ M in the NMR sample and the sparing solubility of the azo-functionalized dendrimers in most solvents. Secondly, the ^{13}C chemical shift approach requires suitable model compounds for comparison of ^{13}C chemical shifts with those of the dendrimers; however very few such model compounds are currently available.

3.2.2. *UV–visible band contour analysis*

The use of UV–visible spectroscopy for study of the tautomeric equilibrium between azo and hydrazone forms requires a knowledge of the molar extinction coefficient of the individual forms. To this end various semiquantitative approaches are usually adopted [21–23].

In the present study, the absorption bands of the two tautomers overlap, such that the resultant broad unresolved band cannot be quantified readily. Therefore, contour analysis was employed to resolve the overlapping bands into their individual components. Band contour analysis, a semiquantitative method used to resolve complex bands in IR, Raman and UV–visible spectra, was

developed in the 1960s [24]. It is an iterative least-squares optimization involving four parameters: peak height, peak position, half-band width and baseline correction. Essentially, the method fits a given function (Lorentzian, Gaussian or some combination) to an experimentally observed band.

The program used for band fitting in the present study was PC116 [25], which is a non-linear least square band fitting procedure. The program PC122 [25] was used in generating components bands. The most important quantity derived from this analysis is the band area of each component band, which is directly related to the concentration of the corresponding tautomer [25]. The PC116 program was used to resolve the bands in the absorption spectra of the dendrimers as well as the model compounds in various solvents. A representative set of resolved absorption spectra is shown in Fig. 7 for the model arylazo dye **2** in TFE.

By using the isosbestic points in Figs. 4 and 5, the resolved bands can be designated as arising from either the azo or hydrazone tautomer. If the resolved bands appear at a wavelength below that of an isosbestic point then they are assigned to the azo tautomer, while bands appearing at a wavelength higher than the isosbestic point are assigned to the hydrazone component. For example, for the phenylazo system (Fig. 7) the resolved bands 1 and 2 are assigned to the azo tautomer component since these bands appear below 548 nm, the isosbestic wavelength for the phenylazo system. Similarly, bands 4–6 are assigned to the hydrazone tautomer since these bands appear above 548 nm. Band 3 was ignored in these assignments since it is located at the isosbestic wavelength.

From the combined band area for the individual tautomers, the ratio of band areas for the azo and hydrazone tautomers could be obtained in the three systems in the form of fractions x_A and x_H. The x_A and x_H data for the dendrimer and model compounds of the three systems in various solvents are summarized in Table 2.

The results in Table 2 show that while there is no clear correlation between tautomer ratio and

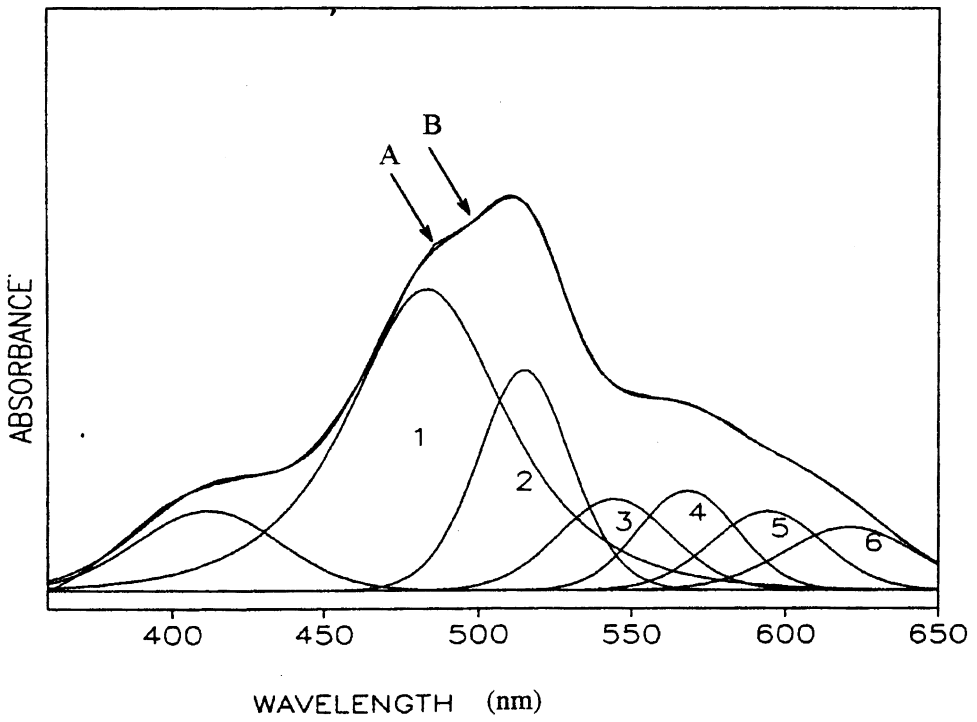


Fig. 7. Observed and resolved UV–visible spectra of the phenylazo model compound **2**: observed (A), re-constituted (B), and resolved spectra from band contour analysis (1–6).

Table 2
Band area ratio for azo tautomer (x_A) and hydrazone tautomer (x_H) for the three types of dyes in various solvents

Solvents	Phenylazo dyes						Naphthalimide azo dyes				Phthalimide azo dyes							
	Model (**2**)		Dendrimer **1-1G**		Dendrimer **1-3G**		Model (**4**)		Dendrimer **3-1G**		Model (**6**)		Dendrimer **5-1G**		Dendrimer **5-2G**		Dendrimer **5-3G**	
	x_A	x_H	x_A	x_H	x_A	x_H	x_A	x_H	x_A	x_H	x_A	x_H	x_A	x_H	x_A	x_H	x_A	x_H
1,4-Dioxane	0.34	0.66	0.41	0.59	0.46	0.54	0.50	0.50	0.54	0.46	0.49	0.51	0.52	0.48	0.49	0.51	0.52	0.48
Toluene	0.35	0.65	0.36	0.64	–	–	0.52	0.48	0.51	0.49	0.37	0.63	0.45	0.55	0.42	0.58	0.46	0.54
Acetone	0.33	0.67	0.42	0.58	0.41	0.59	0.50	0.50	0.55	0.45	0.51	0.49	0.50	0.50	0.50	0.50	0.50	0.50
Acetonitrile	0.32	0.68	0.41	0.59	0.54	0.46	0.49	0.51	0.47	0.53	0.44	0.56	0.47	0.53	0.49	0.51	0.53	0.47
Chloroform	0.29	0.71	–	–	–	–	0.50	0.50	0.53	0.47	0.46	0.54	0.52	0.48	0.52	0.48	0.50	0.50
Ethanol	0.24	0.76	0.43	0.57	0.54	0.46	0.54	0.46	0.63	0.37	–	–	0.51	0.49	0.51	0.49	0.52	0.48
Methanol	0.27	0.73	0.43	0.57	0.56	0.44	0.57	0.43	0.69	0.31	0.48	0.52	0.52	0.48	0.48	0.52	0.47	0.53
Acetic acid	0.43	0.57	0.47	0.53	0.52	0.48	0.56	0.44	0.64	0.36	0.49	0.51	0.54	0.46	0.62	0.38	0.56	0.44
TFE	0.67	0.33	0.53	0.47	0.55	0.45	0.54	0.46	0.73	0.27	0.54	0.46	0.60	0.40	0.60	0.40	0.69	0.31

TFE, 2,2,2-trifluoroethanol.

solvent polarity [26], there is a correlation with the hydrogen bond donor (HBD) properties of the solvent. Thus the band area ratio for the azo tautomer (x_A) can be correlated with the solvent parameter α, a HBD parameter [27]. Our results suggest two key trends between tautomeric behaviour and the solvent parameter for hydrogen bond donors. First, the tautomeric equilibrium shifts toward the azo form in the order: model compound < 1G dendrimer < 2G dendrimer < 3G dendrimer. Second, the proportion of the azo form increases in the order: TFE > aceticacid > MeOH > EtOH > chloroform > acetonitrile > acetone.

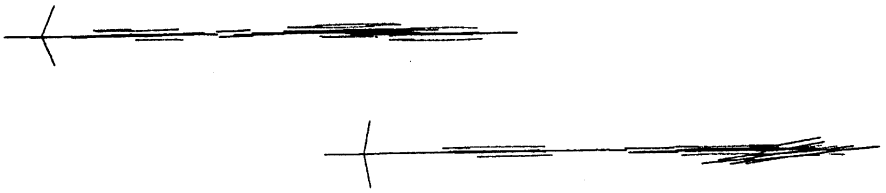
3.3. Rationale of the tautomeric behaviour

It is well known that the various spectroscopic methods used to study azo-hydrazone tautomerism have different advantages and disadvantages and that the results obtained for a given compound can vary with the method employed. This is also true of results involving theoretical studies. For instance, results of an early theoretical study involving azo-hydrazone tautomerism in 1-phenylazo-2-naphthol using the PCILO method indicate that the azo tautomer is strongly favoured over the hydrazone form [28]. This contradicts results from electronic absorption spectra, which suggest that in benzene the tautomers are present in approximately equal amounts [21]. Crystal structure studies are in accord with a predominance of the hydrazone tautomer in the solid state [29]. However, NMR studies indicate that the azo:hydrazone ratio is almost identical in the solid state and in solution [30]. Results from a recent AM1 study [31] show a moderate preference for the azo form and suggest that the observed energy gap between the tautomers is substituent dependent. Similarly, replacement of a phenyl ring by a naphthyl or heterocyclic ring has a marked effect on tautomer stability [31,32].

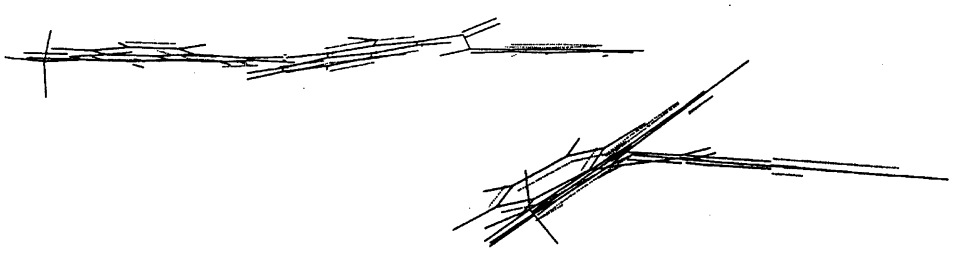
Available literature indicate that the energy difference between azo and hydrazone forms is relatively small and that changes in ring substituents and crystal packing patterns can influence the predominance of one form over the other. It is apparent that data from the phenyl azonaphthol system discussed above cannot be directly extrapolated to our system, which involves a bifurcated H-bond in the hydrazone form. Consequently, the present system provides a unique opportunity to study solvent and quasi-crystal packing effects through the substituted dendrimer scaffold.

Molecular mechanics calculations at the MM2 level have shown that the azo tautomers of model compounds **2**, **4** and **6** are planar (Fig. 8). In contrast, the hydrazone tautomer of model compound **4** is non-planar, presumably because of an interaction between the peri proton of the naphthalimide moiety (cf. H-5′) and the hydrazone proton

(a) Model for the phenylazo derivative (**2**)



(b) Model for naphthalimide azo derivative (**4**)



(c) Model for phthalimide azo derivative (**6**)

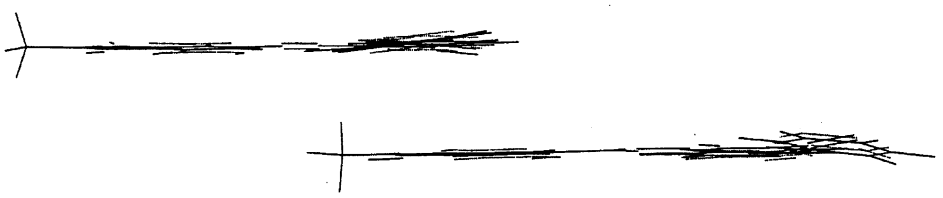


Fig. 8. Hyperchem MM2-generated molecular models for compounds, **2** (a), **4** (b), and **6** (c), with azo form on left and hydrazone form on right.

[33]. This peri interaction is also evident to a small extent in the azo tautomer (Fig. 8b).

Results of our studies have shown that (1) the azo tautomer is preferred over the hydrazone tautomer in the order: model compound < 1G dendrimer < 2G dendrimer < 3G dendrimer and (2) hydrogen bond donating (HBD) solvents shift the equilibrium towards the azo tautomer If one compares the bonding of the azo and hydrazone tautomers in this series, it becomes apparent that the hydrazone tautomer is restricted to H-bonding in an intramolecular sense in order to preserve overall planarity of the conjugated system. In the azo form, the naphthol –OH group can freely rotate and engage in H-bonding without disrupting H-bonding that is critical to molecular planarity. Hence the naphthol –OH group can interact equally well with an HBD solvent or an adjacent π-stacking molecule. Similarly, the presence of more powerful HBD solvents allows the azo form to achieve stabilization through intermolecular H-bonding, without increase in energy due to the loss of planarity in the conjugated system.

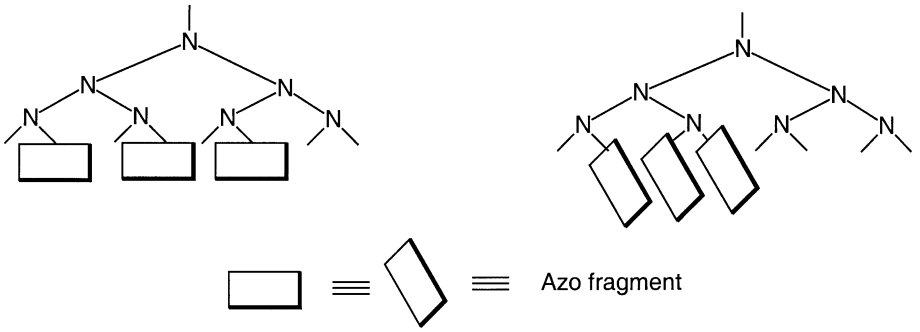


Fig. 9. Possible arrangement of the azo pendant groups on the dendrimer surface.

Since structures **1–3** in the dendrimer series predispose the system toward increased π-stacking because of the density of pendant groups, it is logical that the azo form is progressively preferred as one moves from one model compound to the next, as the dendrimer structures move from **1** to **3**, and as the number of pendant groups increases from 1 to 24. Thus, two possible arrangements of the periphery of the azo moiety can be envisaged in the azo-functionalized dendrimers, *horizontal* or *perpendicular* to the dendnmer surface as illustrated in Fig. 9. Similar arrangements were proposed in a study of starburst dendrimers [34]. It seems reasonable that the arrangement perpendicular to the plane would be favoured, as it would reduce steric crowding. In this regard, the more planar azo tautomer would stack better than the hydrazone form, resulting in the observed increase in the proportion of azo tautomer in dendrimers **2** and **3**.

Acknowledgements

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References

[1] Gregory P. Dyes and Pigments 1986;7:45.
[2] (a) Fischer E, Frei YF. J Chem Soc 1959;31:59.
(b) Reeves RL, Kaiser RS. J Org Chem 1970;35:3670.
[3] Bekarek V, Rothschein K, Vetesnik P, Vecera M. Tetrahedron Lett 1968:3711.
[4] Kishimoto S, Kitahara S, Manabe O, Hiyama H. J Org Chem 1978;43:3882.
[5] Stoyanov S, Antonov L. Dyes and Pigments 1988;10:33.
[6] Berrie AH, Hampson P, Longworth SW, Mathias A. J Chem Soc (B) 1968:1308.
[7] Bekarek V, Dobas J, Socha J, Vetesnik P, Vecera M. Coll Czech Chem Comm 1970;35:1406.
[8] Lycka A, Snobl D, Machacek V, Vecera M. Org Magn Reson 1981;16:17.
[9] Lycka A, Snobl D, Machacek V, Vecera M. Org Magn Reson 1981;15:390.
[10] Cheon K-S, Kazmaier PM, Keum S-R, Buncel E. [in preparation].
[11] Burawoy A, Thompson AR. J Chem Soc 1953:1443.
[12] Lycka A, Necas M, Jiman J, Straka J, Schneider B. Collect Czech Chem Commun 1990;55:193.
[13] Ball P, Nicholls CH. Dyes and Pigments 1982;3:5.
[14] Kostyuchenko EE, Traven VF, Mkhitarov RA, Menshikova NF, Stepanov BI. Zh Org Khim 1979;15:884.
[15] Law K-Y, Kaplan S, Crandall R, Tamawskyj IW. Chem Mater 1993;5:557.
[16] Kelemen J, Moss S, Sauter H, Winkler T. Dyes and Pigments 1982;3:27.
[17] Connor J, Fine DJ, Price R. J Chem Soc Dalton Trans 1981:559.
[18] Velusamy P, Pitchumani K, Snnivasan C. Tetrahedron 1996;52:3487.
[19] Gottlieb HE, Kotlyar V, Nudelman A. J Org Chem 1997; 62:7512.
[20] Kalinowski H-O, Berger S, Braun S. Carbon-13 NMR spectroscopy. London: John Wiley & Sons; 1988.
[21] Kishimoto S, Kitahara S, Manabe O, Hiyama H. J Org Chem 1978;43:3882.
[22] Burawoy A, Salem AG, Thompson AR. J Chem Soc 1952: 4793.
[23] Saeva FD. J Org Chem 1971;36:3842.
[24] (a) Pitha J, Jones RN. Can J Chem 1966;44:3031;
(b) Pitha J, Jones RN. Can J Chem 1967;45:2347;
(c) Seshadri KS, Jones RN. Spectrochim Acta 1963;19:1013;
(d) Jones RN. Computers in chemistry and instruction, vol. 7. Marcel Dekker Inc.; 1977. p. 1.

[25] Jones RN, Pitha J. NRC (Natl Res Counc Can) 1968 [Bull. Nos. 11 and 12].
[26] Antonov L, Stoyanov S, Stoyanova T. Dyes and Pigments 1995;27:133.
[27] (a) Reichardt C. Solvents and solvents effects in organic chemistry. 2nd ed. Weinheim: VCH; 1990.
(b) Buncel E, Rajagopal S. Acc Chem Res 1990;23:226.
(c) Liu PC, Hoz S, Buncel E. Gazz Chim Ital 1996;126:31.
[28] Goursot A, Jacques P, Faure J. Chem Phys 1977;20:319.
[29] Monahan AR, Flannery JB. Chem Phys Lett 1972; 17:510.
[30] Lycka A, Jirman J, Schneider B, Straka J. Magn Reson Chem 1988;26:507.
[31] Morley JO. J Phys Chem 1994;98:1818.
[32] Cox RA, Buncel E. The chemistry of the hydrazo, azo and azoxy groups. In: Patai S, Ropopport Z, editors. The chemistry of functional groups, vol. 2. London: Wiley, 1997.
[33] Desiraju GR. Crystal engineering. The design of organic solids. Amsterdam: Elsevier, 1989 [chapters 4, 5 and 6].
[34] Jockusch S, Turro NJ, Tomalia DA. Macromolecules 1995;28:7416.