

# A Substituent Correlation and Medium Effects on the Annular Tautomerism of Substituted 5-Aryltetrazoles: the Nitrogen Analogues of Benzoic Acids. A Carbon-13 N.m.r. and Dipole Moment Study

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The annular tautomerism of substituted 5-phenyltetrazoles shows a linear correlation of  $\log K_T$  ( $K_T = [N(1)H]/[N(2)H]$ ) with the Hammett  $\sigma$  values of *para*-substituents. The tautomerism favours the 1*H*-form but electron-withdrawing substituents displace the equilibrium towards the 2*H*-form. Solvent dielectric permittivity and temperature effects also influence the annular tautomerism. A change of solvent from dimethyl sulphoxide to dioxane and an increase in temperature had similar effects in orienting the tautomerism towards the 2*H*-form, but the temperature effect was relatively small. Carbon-13 n.m.r. shifts and dipole moment analyses of the tautomerism gave complementary results.

The tetrazole ring ( $-CN_4H$ ) [the nitrogen valence analogue of the carboxy group ( $-CO_2H$ )] exhibits biological activity in many compounds. This activity is related to that of the corresponding carboxylic acid.<sup>2</sup> Aryltetrazoles, the analogues of benzoic acids, generally exhibit depressant activity on the central nervous system.<sup>3</sup> A structural difference between  $-CN_4H$  and  $-CO_2H$  is the possibility of two tautomeric forms [(1) and (2)] in the former case. Until recently the 2*H*-form (2) was generally considered to be the dominant form of 5-aryltetrazoles, but n.m.r. studies<sup>4</sup> of a few derivatives in dimethyl sulphoxide at 23 °C, and a dipole moment study<sup>5</sup> of 5-*p*-tolyltetrazole in dioxane at 30 °C, showed that the 1*H*-form (1) was preferred. Increasing interest<sup>2</sup> in the biological activity changes which may be induced by replacing carboxy groups of active molecules with tetrazolyl groups makes a knowledge of the effects of substituent and medium on the tautomerism (1)  $\rightleftharpoons$  (2) of particular importance.

## Results and Discussion

(a) *Substituent Effects.*—The annular tautomerism of a series of *para*-substituted 5-aryltetrazoles in dimethyl sulphoxide is summarized in Table 1. The tetrazole C-5 chemical shifts of the parent compounds, along with those of their 1- and 2-*N*-methyl isomers, were used to determine the composition of the tautomeric mixture. We have previously commented on the approximations involved in this approach.<sup>6</sup> The data exhibit an excellent linear correlation of the logarithm of the tautomerism constant  $K_T$  (Table 1) with the Hammett  $\sigma$  values of substituents (Figure 1).

The correlation shows that substituent electron donation towards the tetrazole ring favours the 1*H*-form, whilst electron withdrawal favours the 2*H*-form.

Interannular conjugation in both tautomers of 5-aryltetrazoles involves contributions from canonical forms of types A and B<sup>6-8</sup> (Figure 2). Although 1*H* tautomers may be less planar than the 2*H*-forms the A-type interannular conjugation should make a greater contribution in the 1*H* tautomer, since it involves two canonical forms as against one for the 2*H* tautomer. The contribution of the B-type canonical forms should also be greater in the 1*H* tautomer, where there is less charge separation. The origin of the observed substituent effect on the annular tautomerism is best explained by conjugation of type A. The importance of this A-type conjugation is suggested from the relationship of dipole

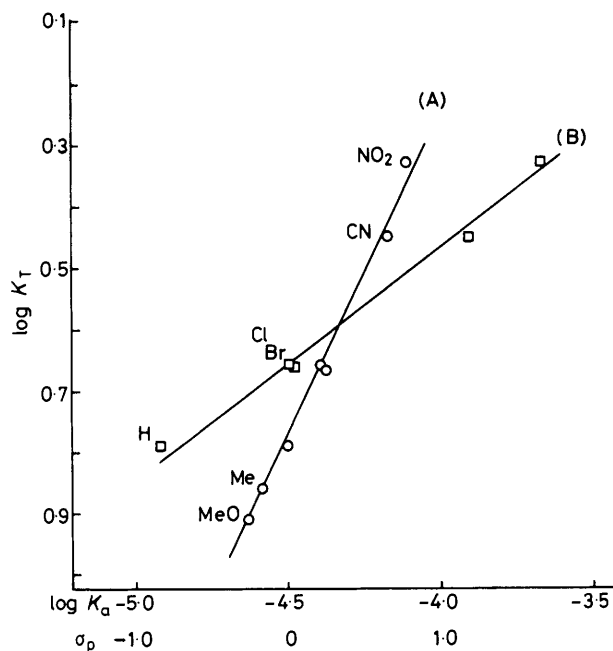
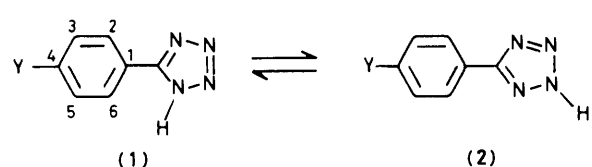


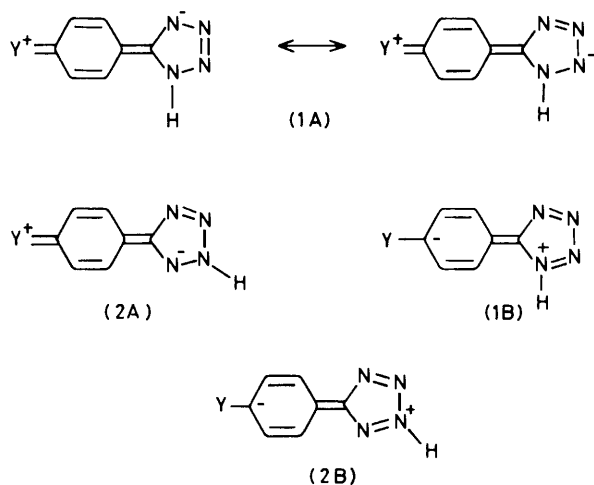
Figure 1. (A) Plot of  $\log K_T$  in  $(CD_3)_2SO$  versus Hammett  $\sigma_p$  values (ref. 10); (B) Plot of  $\log K_T$  in  $(CD_3)_2SO$  versus  $\log K_a$  in 75%  $Me_2SO$  (from ref. 7)

moment directions for the 1*H*- and 2*H*-tautomers<sup>9</sup> with the observed expected increase on passing from 1,5-dimethyltetrazole ( $\mu$  5.30 D) to 1-methyl-5-phenyltetrazole ( $\mu$  5.70 D) and the expected absence of such a change on passing from 2,5-dimethyltetrazole ( $\mu$  2.42 D) to 2-methyl-5-(*p*-tolyl)tetrazole ( $\mu$  2.41 D). Hence the population of the 1*H*-tautomer should be increased by electron-donating and decreased by

**Table 1.** Tetrazole C-5 shifts (p.p.m. from Me<sub>4</sub>Si) in (CD<sub>3</sub>)<sub>2</sub>SO <sup>a</sup>

<i>p</i> -Substituent on 5-Ph	Parent	1-Me derivative	2-Me derivative	1 <i>H</i> -form (%)	<i>K</i> <sub>T</sub>	log <i>K</i> <sub>T</sub>	Hammett $\sigma_p$ values <sup>b</sup>
MeO	154.8	153.7	164.1	89	8.09	0.91	-0.268
Me	155.3	154.1	164.3	88	7.33	0.86	-0.170
H	155.6	154.2	164.2	86	6.14	0.79	0
Cl	154.9	153.1	163.3	82	4.56	0.66	0.227
Br	155.1	153.3	163.3	82	4.56	0.66	0.232
CN	155.4	152.9	162.7	74	2.85	0.45	0.660
NO <sub>2</sub>	155.8	152.7	162.5	68	2.12	0.33	0.778

<sup>a</sup> All solutions 0.5M; measurements made at 23 ± 1 °C. <sup>b</sup> From ref. 10.



**Figure 2.** Canonical structures for 1*H*- and 2*H*-tautomers of 5-aryltetrazoles with an electron-donating *para*-substituent (structures with a positive charge at the *para*- and *ortho*-phenyl carbon atoms and structures with a negative charge at the *ortho*-phenyl carbon atoms are omitted)

electron-withdrawing *para*-substituents owing to their influence on the A-type conjugation, and the substituent effect can be correlated with the Hammett  $\sigma_p$  values <sup>10</sup> of the substituents. Interestingly the observed substituent effects agree with a prediction previously made <sup>11</sup> by using 4- and 5-substituted 1-methylimidazolium ions as models for the ionization of 1*H*- and 2*H*-tetrazole tautomers. The acid dissociation constants of the 5-aryltetrazoles have recently <sup>7</sup> been shown to exhibit a linear correlation with Hammett  $\sigma$  values, and hence the present data indicate a linear correlation between the logarithms of the tautomeric constant and acid dissociation constant *K*<sub>a</sub> for the 5-aryltetrazole series (Figure 1). These correlations will be of value for structure-activity studies of biological activity in the tetrazole series.

(b) *Solvent Effects.*—The tautomeric equilibrium of tetrazole itself in solution lies strongly towards the 1*H*-form. <sup>9,12-14</sup> There is little difference in energy between the two forms of tetrazole and in the gas phase both are present, with the 2*H*-form dominant. <sup>9,13,14</sup> The predominance of the 1*H*-form in dioxane solution at 30.0 °C (78% 1*H*) has been explained <sup>9</sup> in terms of greater Onsager solvent reaction-field stabilization of the more polar form. <sup>15</sup> The dipole moments in the gas phase of *C*-deuterio-1*H*-tetrazole and -2*H*-tetrazole are 5.30 and 2.19 D, respectively, by microwave spectroscopy; <sup>14</sup> that of tetrazole in dioxane is 4.88 D, <sup>9</sup> and the dioxane values for 1*H*- and 2*H*-forms of tetrazole can be equated to those, measured in benzene, of 1,5-dimethyltetrazole (5.31 D) or 1-ethyltetra-

zole (5.53 D) and of 2,5-dimethyltetrazole (2.42 D), for reasons given in ref. 9.\* The C-5 chemical shifts of tetrazole (142.1–144.2), 1-methyltetrazole (143.4–145.4), and 2-methyltetrazole (151.9–153.5) indicated a relative insensitivity to solvent and a predominance of the 1*H*-form in a range of solvents of varying polarity including water, <sup>12</sup> dimethyl sulphoxide, <sup>12,13</sup> and dioxane. <sup>12</sup> With a bulky aromatic substituent at the tetrazole 5-position there are significant differences from the case of tetrazole; ring conformations and interannular conjugation in 5-aryltetrazoles should give rise to differences in energies and solvation effects between the two forms. We have now observed a large influence of solvent dielectric permittivity on the annular tautomerism of the 5-aryltetrazoles. Earlier dipole moment studies on 5-*p*-tolyltetrazole and its 1-*N*-Me and 2-*N*-Me derivatives in (non-polar) dioxane have indicated a much higher dipole moment for the 1*H*- than for the 2*H*-form. <sup>5</sup> Table 2 contains a comparison of the tautomerism in dimethyl sulphoxide ( $\epsilon$  49) and dioxane ( $\epsilon$  2.2). Carbon-13 n.m.r. data measured in both solvents clearly show a strong preference for the more polar 1*H*-form in dimethyl sulphoxide. The very low solubility of the parent *para*-substituted 5-aryltetrazole in dioxane limited the range of compounds which could be studied by carbon n.m.r., but the effect was clearly observed in each case (Table 2, nos. 1–3) for which the C-5 signals could be detected in both dimethyl sulphoxide and dioxane. Results on the tautomerism in dioxane (Table 2, nos. 1,3,4, and 5) also illustrate the influence of decreasing solvent dielectric permittivity in shifting the tautomerism towards the 2*H*-form. In those cases (Table 2) where the tautomerism could be measured in dioxane by the carbon-13 n.m.r. method and independently by the dipole moment method there is a satisfactory agreement between the results when allowance is made for the necessary approximations involved. <sup>5,6</sup>

Weakly acidic 5-aryltetrazoles as solutes in a weakly basic solvent such as dimethyl sulphoxide (*T*) and dioxane (*D*) probably exist in two tautomeric N–H ⋯ O (solvent) hydrogen-bonded forms (1-*H* ⋯ solvent) and (2-*H* ⋯ solvent). <sup>13</sup>C N.m.r. spectra in (CD<sub>3</sub>)<sub>2</sub>SO and in [2H<sub>6</sub>]dioxane, therefore, refer to the tetrazole ⋯ solvent complex. The dipole moment of a weakly acidic compound measured in dioxane as solvent corresponds to the value of the solute ⋯ dioxane hydrogen-

\* In ref. 9, on pp. 285 and 288, respectively, the dipole moments of 1-methyl-5-(*p*-chlorophenyl)tetrazole and 2-methyl-5-(*p*-chlorophenyl)tetrazole should read 4.76 D (and not 4.59 D) and 3.16 D (and not 3.03 D), respectively. It then follows that the dipole moment of 1-methyl-5-phenyltetrazole (5.73 D) acts at  $\tau = 46^\circ$  (not  $38^\circ$ ) to the Ph–C(5) bond axis, that is at  $\theta = 66^\circ$  (not  $58^\circ$ ) to the reference *X*-axis. Similarly, the dipole moment of 2-methyl-5-(*p*-tolyl)tetrazole (2.42 D) makes an angle ( $\tau$ ) of  $92^\circ$  (not  $87^\circ$ ) with the Ph–C(5) bond axis, and hence an angle ( $\theta$ ) of  $36^\circ$  (not  $30^\circ$ ) with the *X*-axis; the derived angle  $\theta$  for 2-methyl-5-phenyltetrazole (not studied) would then be  $45^\circ$ , and not  $40^\circ$ .

**Table 2.** Solvent effects on annular tautomerism of substituted 5-phenyltetrazoles

No.	Substituent(s) on 5-Ph	Solvent	C-5 Shifts (p.p.m. from Me <sub>4</sub> Si) <sup>a,b</sup>				$\mu/D$			
			Parent <sup>b</sup>	1-Me	2-Me	1-H (%)	Parent <sup>d</sup>	1-Me <sup>f</sup>	2-Me <sup>f</sup>	1-H (%) <sup>g</sup>
1	2,6-Cl <sub>2</sub>	{(CD <sub>3</sub> ) <sub>2</sub> SO	151.4	150.6	159.9	91	5.20 <sup>e</sup>	6.69	2.51	54
		{[ <sup>2</sup> H <sub>8</sub> ]Dioxane	154.4	151.3	161.0	68				
2	2-Me	{(CD <sub>3</sub> ) <sub>2</sub> SO	155.35	153.85	164.6	86	5.20 <sup>e</sup>	6.69	2.51	54
		{[ <sup>2</sup> H <sub>8</sub> ]Dioxane	157.6	154.6	165.8	73				
3	4-MeO	{(CD <sub>3</sub> ) <sub>2</sub> SO	154.8	153.7	164.1	89	5.32 <sup>e</sup>	6.08	2.56	72
		{[ <sup>2</sup> H <sub>8</sub> ]Dioxane	158.8 <sup>c</sup>	154.6 <sup>c</sup>	165.6 <sup>c</sup>	64				
4	4-Cl	{(CD <sub>3</sub> ) <sub>2</sub> SO	154.9	153.1	163.2	82	4.26 <sup>e</sup>	4.76	3.16	64
		{[ <sup>2</sup> H <sub>8</sub> ]Dioxane	155.3	154.1	164.3	88				
5	4-Me	{(CD <sub>3</sub> ) <sub>2</sub> SO	155.3	154.1	164.3	88	4.99 <sup>e</sup>	6.03	2.41	62 <sup>h</sup>
		{[ <sup>2</sup> H <sub>8</sub> ]Dioxane								

<sup>a</sup> At 23 ± 1 °C unless otherwise indicated. <sup>b</sup> Concentrations in the range 0.25–0.50M. <sup>c</sup> At 70 °C. <sup>d</sup> In normal dioxane at 30.0 °C. <sup>e</sup> Maximal weight fractions of the solute in dioxane, 0.11, 0.009, 0.011, and 0.003 for nos. 1, 3, 4, and 5, respectively. <sup>f</sup> Measured in benzene at 30.0 °C. <sup>g</sup> Calculated by solving  $^5\mu^2(\text{parent}) = x\mu^2(1\text{-Me}) + (1-x)\mu^2(2\text{-Me})$ . <sup>h</sup> Ref. 5.

bonded complex,<sup>16,17</sup> because dioxane is non-polar in the gaseous phase<sup>18</sup> and exhibits a low dipole moment (0.08 D) as a liquid.<sup>19</sup> The [1H]/[2H] tautomeric ratios in the solvent *S* (*T* or *D*), which refers to the tetrazole...solvent complex, are (for *T* and *D*, respectively) 91/9 and 68/32 (or 54/46), 86/14 and 73/27, 89/11 and 64/36 (or 72/28), 82/18 and 64/36, and 88/12 and 62/38 for the 5-aryltetrazoles (1–5) listed in Table 2, indicating that the N(1)H population is markedly less in dioxane.

For a given tetrazole, the strength of the hydrogen bonding in [N(1)H...*S*] and [N(2)H...*S*] tautomers may differ, and depend on the solvent. In a specified solvent, the strengths of the hydrogen bonding in the tautomers should also depend on the relevant acid strength of the particular tetrazole.

In a dense medium the dipole moment of a polar solute interacts with Onsager's solvent reaction field,<sup>15</sup> giving rise to a stabilization of the species whose energy content becomes  $E = E_{\text{gas}} + E_s$ ,  $E_s$  being defined in equation (i), where  $\epsilon_s$  designates

$$E_s = \left( \frac{\epsilon_s - 1}{2\epsilon_s + 1} \right) \frac{\mu_s^2}{a^3} = (1/a^3) F(\epsilon_s) M_s \quad (i)$$

the solvent dielectric permittivity (49) for dimethyl sulphoxide (*T*) and 2.2 only for dioxane (*D*),  $\mu_s$  the dipole moment of the solute (in the solvent *S*) and  $a$  its molecular radius.

For a given tetrazole in the solvent *S*, the  $E_s$  term is not the same for both tautomers and, since  $M_s[\text{N}(1)\text{H}...S]$  is much greater than  $M_s[\text{N}(2)\text{H}...S]$  (see below), the [N(1)H...*S*] form is more favoured as the  $\Delta M_s$  value is greater (the  $a^3$  term is similar for the two tautomeric forms). In addition, the  $F(\epsilon_s)$  term is much greater for the solutions in dimethyl sulphoxide:  $F(49) = 0.49$  as against  $F(2.2) = 0.22$ .

A comparison of the solvation effects on a given tetrazole as a solute in dimethyl sulphoxide and in dioxane needs the relevant  $\Delta M_s$  values. The dipole moments of [N(1)H...*D*] and [N(2)H...*D*] tautomers can be equated to those of the corresponding 1-N-Me and 2-N-Me isomers,<sup>5,9</sup> mainly because dioxane is non-polar. The corresponding figures for [N(1)H...*T*] and [N(2)H...*T*] tautomers might be estimated from the preceding values, as vectors, by adding the dipole moment of dimethyl sulphoxide (3.96 D in the gaseous state<sup>20</sup>) along the acidic H-N bond axis. Because of the predicted directions of the 5-aryltetrazole 1H and 2H dipole moments<sup>9</sup> (see footnote, p. 722) the  $\Delta M_T$  term is predicted to be much higher than the  $\Delta M_D$  term for a given 5-aryltetrazole. It then follows that both the  $F(\epsilon_s)$  and  $\Delta M_s$  terms should, as observed, favour the 1-H tautomeric form in dimethyl sulphoxide more than in dioxane.

**Table 3.** Influence of temperature on annular tautomerism of 5-phenyltetrazole in (CD<sub>3</sub>)<sub>2</sub>SO<sup>a</sup>

Temp. (°C)	C-5 Shifts <sup>b</sup>			1H- form (%)
	Parent	1-Me	2-Me	
33	155.48	154.0	164.20	85.4
43	155.55	154.0	164.25	84.8
53	155.68	154.0	164.25	83.6
63	155.81	154.05	164.32	82.8
73	156.00	154.12	164.32	81.5
84	156.07	154.12	164.38	80.9
96	156.26	154.12	164.45	79.3

<sup>a</sup> All concentrations 0.5M. <sup>b</sup> Identical shifts were obtained at these temperatures using 1M-solutions also.

However, despite the rather large differences in the  $\Delta M_s$  values for the 5-aryltetrazoles nos. 1, 5, 3, and 4 quoted in Table 2 ( $\Delta M_D = 38.4, 30.6, 30.4,$  and  $12.7 \text{ D}^2$ ;  $\Delta M_T$  values greater but in the same order), indicating a different solvation effect on passing from the gas value to the solution value (in (CD<sub>3</sub>)<sub>2</sub>SO or [<sup>2</sup>H<sub>8</sub>]dioxane), a good linear correlation of the logarithm of the tautomeric constant  $K_T$  with the Hammett  $\sigma_p$  values of substituents is observed. This shows that the substituent effect on 5-aryltetrazoles outweighs the solvent effect.

(c) *Temperature Effects.*—The influence of temperature on the annular tautomerism of 5-phenyltetrazole in dimethyl sulphoxide in the range 33–96 °C is shown in Table 3. The effect observed for 0.5M- and 1.0M-solutions was relatively weak. The higher temperatures changed the equilibrium slightly towards the less polar 2H-form. The changes in the solvation effect with increasing temperature arise from an overall disruption of self-associated species and of the more abundant solute-solvent hydrogen-bond complexes. A shift towards the 2H-form with increasing temperature is consistent with the solvent sensitivity already observed and also with observations of a preference for the 2H-form in the vapour phase.<sup>9,14</sup>

### Experimental

<sup>13</sup>C N.m.r. spectra were measured using Me<sub>4</sub>Si as internal reference with a JEOL FX-60 spectrometer and JNM-VT temperature controller. Temperatures (±1 °C) were monitored with a Comark Digital thermometer 5 000 and checked with a methanol proton probe.

The synthesis of the parent 5-aryltetrazoles and direct

Table 4. Physical data from dipole moment determinations at 30.0 °C

Compound	Solvent	$w_{\max}$	$\alpha_0$	$-\beta$	$P_{2\infty}$	$R_D$	$\mu/D$
5-(2,6-Dichlorophenyl)tetrazole	Dioxane	0.011	15.50 <sup>a</sup>	0.320	593.4	49.3	5.20
5-(2,6-Dichlorophenyl)-1-methyltetrazole	Benzene	0.012	20.85	0.464	953.6	54.0	6.69
5-(2,6-Dichlorophenyl)-2-methyltetrazole	Benzene	0.008	3.05	0.447	180.5	54.2	2.51
5-(4-Methoxyphenyl)tetrazole	Dioxane	0.009	19.73 <sup>b</sup>	0.219	614.9	46.1	5.32
5-(4-Methoxyphenyl)-1-methyltetrazole	Benzene	0.009	20.70	0.350	792.9	50.8	6.08
5-(4-Methoxyphenyl)-2-methyltetrazole	Benzene	0.007	3.80	0.340	183.0	51.0	2.56
5-(4-Chlorophenyl)tetrazole	Dioxane	0.015	12.46 <sup>c</sup>	0.267	410.0	44.3	4.26
5-(4-Chlorophenyl)-1-methyltetrazole	Benzene	0.006	12.26	0.240	505.7	49.0	4.76
5-(4-Chlorophenyl)-2-methyltetrazole	Benzene	0.010	5.32	0.240	249.8	49.2	3.16

<sup>a</sup>  $\alpha = 15.5 + 115 w$ . <sup>b</sup>  $\alpha = 19.73 + 110 w$ . <sup>c</sup>  $\alpha = 12.46 - 8 w$ .

methylations of the tetrazole anions were carried out by methods previously described.<sup>21</sup> The 1-methyl- and 2-methyl-5-aryltetrazoles were separated by column chromatography on silica gel or by fractional crystallizations. All the compounds examined gave satisfactory microanalytical data and their structures were proved by n.m.r. spectroscopy. New compounds and those not previously reported by us include 5-(4-bromophenyl)tetrazole, m.p. 261 °C (from acetic acid) (lit.,<sup>7</sup> 267–269 °C) (Found: C, 37.5; H, 2.25; N, 24.95. Calc. for C<sub>7</sub>H<sub>5</sub>BrN<sub>4</sub>: C, 37.3; H, 2.2; N, 24.9%); 1-methyl-5-(4-bromophenyl)tetrazole, m.p. 143–144 °C (from aqueous ethanol) (Found: C, 40.05; H, 3.1; N, 23.6. C<sub>8</sub>H<sub>7</sub>BrN<sub>4</sub> requires C, 40.15; H, 2.95; N, 23.45%); 2-methyl-5-(4-bromophenyl)tetrazole, m.p. 124–126 °C (needles from ethanol) (Found: C, 40.3; H, 3.1; N, 23.3%); 5-(4-cyanophenyl)tetrazole, m.p. 188–189 °C (lit.,<sup>7</sup> 188–189 °C) (from aqueous ethanol) (Found: C, 56.3; H, 3.0; N, 40.6. Calc. for C<sub>8</sub>H<sub>5</sub>N<sub>5</sub>: C, 56.15; H, 2.9; N, 40.95%); 1-methyl-5-(4-cyanophenyl)tetrazole, m.p. 154–156 °C (from ethanol) (Found: C, 58.45; H, 3.75; N, 37.75. C<sub>9</sub>H<sub>7</sub>N<sub>5</sub> requires C, 58.4; H, 3.8; N, 37.85%); 2-methyl-5-(4-cyanophenyl)tetrazole, m.p. 126–128 °C (from ethanol) (Found: C, 58.2; H, 3.8; N, 38.1%); 5-(4-methoxyphenyl)tetrazole, m.p. 232–233 °C (needles from acetic acid) (lit.,<sup>7</sup> 232–233 °C) (Found: C, 54.4; H, 4.55; N, 32.0. Calc. for C<sub>8</sub>H<sub>8</sub>N<sub>4</sub>O: C, 54.5; H, 4.55; N, 31.8%); 1-methyl-5-(4-methoxyphenyl)tetrazole, m.p. 118 °C (needles from ethanol) (Found: C, 56.5; H, 5.45; N, 29.5. C<sub>9</sub>H<sub>10</sub>N<sub>4</sub>O requires C, 56.8; H, 5.25; N, 29.5%); 2-methyl-5-(4-methoxyphenyl)tetrazole, m.p. 85–86 °C (Found: C 56.6; H, 5.3; N, 29.7%); 1-methyl-5-(4-chlorophenyl)tetrazole has m.p. 120–122 °C (lit.,<sup>4</sup> value 89–90 °C misquoted).

**Dipole Moment Measurements.**—Cryoscopic benzene R.P. and Normapur dioxane R.P. (both from Prolabo, Paris), were twice recrystallized and dried over metallic sodium: at 30.0 °C for benzene  $d_4 = 0.8687$ ,  $n_D = 1.4950$ , and  $\epsilon = 2.2642$  (referred to best literature value, 2.2741 at 25 °C); for dioxane  $d_4 = 1.0227$ ,  $n_D = 1.4175$ ,  $\epsilon = 2.2055$ .

The electric dipole moments were determined in the specified non-polar solvent at 30.0 °C by using the well known Debye refractivity method. The total polarization of the solute, extrapolated to infinite dilution, was calculated from the ratios<sup>22</sup> (ii) and (iii) where  $w$  is the weight fraction of the

$$\alpha_0 = \lim_{(w=0)} \left( \frac{\epsilon - \epsilon_1}{w} \right) \quad (\text{ii}) \quad \beta = \frac{\sum(v - v_1)}{\sum w} \quad (\text{iii})$$

solute, and  $\epsilon$  and  $v$  are the dielectric permittivity and specific volume of the solution, respectively; subscript one refers to the pure solvent as used, *i.e.* made up in the same way as the solutions. The  $\alpha_0$  value was calculated from the linear function

$\alpha = \alpha_0 + \alpha'w$ , obtained by least-squares analysis of the  $\epsilon(w)$  polynomial (quadratic) function.

The distortion polarization of the solute,  ${}_E P + {}_A P$ , was assumed to equal the molar refraction ( $R_D$ ) calculated from the experimental values determined in solutions of 5-*p*-(tolyl)tetrazole, 1-methyl-5-(*p*-tolyl)tetrazole, and 2-methyl-5-(*p*-tolyl)tetrazole (44.3, 49.0, and 29.2 cm<sup>3</sup>),<sup>5</sup> and from the experimental refractions of chlorobenzene (31.14 cm<sup>3</sup>), or anisole (32.88 cm<sup>3</sup>),<sup>23</sup> and of benzene (26.18 cm<sup>3</sup>).

The dielectric permittivities of the solvent and solutions, referred to that of benzene, were measured with a W.T.W. Dipolmeter DM 01 (from Weilheim Oberbayern, West Germany), by using a thermostatted DFL 2 cell adequately modified.<sup>24</sup> The specific volumes were accurately measured with a Digital Microdensimeter DMA O2C (from Anton Paar KG, Graz, Austria), and the refraction indices with a VEB Carl Zeiss interferometer (from Jena, DDR).<sup>25,26</sup>

At least ten dilute dioxane solutions of 5-(2,6-dichlorophenyl)tetrazole, 5-(4-methoxyphenyl)tetrazole, and 5-(4-chlorophenyl)tetrazole were examined; for the *N*-methylated derivatives the number of benzene solutions studied was six.

For each solute examined, the values of  $w_{\max}$  (given to only three decimal places, though it is known to five or six),  $\alpha_0$ ,  $\beta$  (cm<sup>3</sup> g<sup>-1</sup>),  $P_{2\infty}$  and  $R_D$  (both cm<sup>3</sup> mol<sup>-1</sup>), and  $\mu$  (Debye) are given in Table 4.

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Received 18th April 1983; Paper 3/613