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The electric dipole moment of 5-(*p*-tolyl)tetrazole in dioxane at 30.0° (4.99 D) suggests that the compound is a mixture of the 1*H*-tautomer (60 ± 10%) and the 2*H*-tautomer (40 ± 10%) in this medium. This determination was made by taking $\mu(2H)$ as $\mu(2Me) = 2.41$ D in benzene, and by taking $\mu(1H)$ as $\mu(1Me) = 6.03$ D in benzene with due allowance being made for the presence of interannular conjugation in the 1*H*-tautomer but not in the 1-methyl isomer. The dipole moments of 1-methyl-5-(*p*-tolyl)tetrazole and 2-methyl-5-(*p*-tolyl)tetrazole were also measured in dioxane; that of 1,5-trimethylenetetrazole was measured in benzene. Comparison with relevant data for unsubstituted tetrazole has also been made.

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Introduction.

Tetrazoles are known to exhibit activity on the central nervous system. Contrary to aliphatic substituents which generally confer convulsant activity on the compound, aromatic substituents tend to give depressant activity (1). Because of the increasing interest in replacing the carboxyl group of biologically active molecules with the tetrazole group (2-5), a knowledge of the influence of a 5-substituent on the annular tautomerism in tetrazole is particularly important.

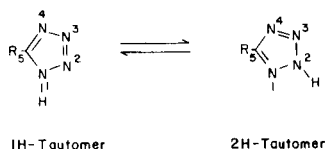


Figure 1

1*H*- and 2*H*-Tautomers for Tetrazole (R = H)
and 5-(*p*-Tolyl)tetrazole (R = *p*-MeC₆H₄)

The problem of annular tautomerism (1*H* ⇌ 2*H*) in unsubstituted tetrazole has been examined by various methods (6,7), including nmr spectroscopy, dipole moments measurements and theoretical calculations, with the general conclusion that the 1*H*-tautomer strongly predominates (Figure 1).

From ¹³C nmr spectroscopy in DMSO-water (4:1 v/v), with *N*-methyltetrazoles (1-methyl and 2-methyl) as models for the individual tautomers, the (1*H*)/(2*H*) tautomer percent ratios were found to be 93:7, 55:45, 48:52 and 86:14 for 5-amino-, 5-methyl-, 5-chloro and 5-phenyltetrazole, respectively (8). The tautomeric 1*H*-form is also preferred for 5-phenyl-, 5-(*p*-tolyl)-, 5-(*o*-nitrophenyl)- and 5-(*p*-nitrophenyl)tetrazole in DMSO-water (83:17 v/v) (9). As these results refer to media of very high dielectric permittivity [roughly calculated to attain 55, from $\epsilon(\text{DMSO}) = 49$ and $\epsilon(\text{water}) = 80$], and high basicity, it seemed of interest to

examine annular tautomerism in a 5-aryltetrazole in a medium of low dielectric permittivity, and weak basicity, for example dioxane, whose ϵ -value is only 2.2. In the present case, since the 1*H*- and 2*H*-tautomers can form a hydrogen-bonded complex with the solvent if it is basic, not only the solvent ϵ -factor plays a role (10), as for example in the conformational ratio of 2-formylfuran (11), where there is no complexation with basic solvents.

In this work, the electric dipole moments of 5-(*p*-tolyl)tetrazole (I), 1-methyl-5-(*p*-tolyl)tetrazole (II), 2-methyl-5-(*p*-tolyl)tetrazole (III), and 1,5-trimethylenetetrazole (IV) (Figure 1), were measured in benzene and/or dioxane at 30.0°, and an attempt has been made to determine the (1*H*)/(2*H*) tautomer percent ratio for 5-(*p*-tolyl)tetrazole in dioxane as a solvent. Results are listed Table I, which also includes dipole moments of some tetrazoles taken from the literature. This is the first reported attempt to measure the tautomer percent ratio for a 5-aryltetrazole by the dipole moment method.

Results and Discussion.

The quadratic dipole moment of potentially tautomerizable 5-(*p*-tolyl)tetrazole in dioxane can be quantified by the simple expression:

$$\mu^2 = x \cdot \mu^2(1H) + (1 - x) \cdot \mu^2(2H)$$

where $\mu(1H)$ and $\mu(2H)$, respectively, designate the dipole moments in dioxane of 1*H*-5-(*p*-tolyl)tetrazole and 2*H*-5-(*p*-tolyl)tetrazole. Since these dipole moments cannot be measured, it has been assumed that they can be taken as equal to those of 1-methyl-5-(*p*-tolyl)tetrazole (II) and 2-methyl-5-(*p*-tolyl)tetrazole (III) in benzene or dioxane. Such a hypothesis is justified by the following.

a.

By analogy with what is observed for 1*H*-tetrazole and 2*H*-tetrazole, the dipole moments of 1*H*-5-(*p*-tolyl)tetrazole and 2*H*-5-(*p*-tolyl)tetrazole should vary considerably in magnitude, by at least 3.2 D. Further, the dipole moments

Table I
Experimental Dipole Moments of Various Tetrazoles (Debye Units)

Compound (a)	μ (gas) (d)	μ (benzene) (e)	μ (dioxan) (e)
1 <i>H</i> -tetrazole (b)	5.30 (12)	—	—
2 <i>H</i> -tetrazole (b)	2.14 (12)	—	—
tetrazole (gas) (c)	2.19 (12)	—	—
1 <i>H</i> -tetrazole \rightleftharpoons 2 <i>H</i> -tetrazole	—	—	5.11 (13) (f), 4.91 (14)
1-methyltetrazole	—	5.38 (13) (f)	—
1-ethyltetrazole	—	5.46 (13)	—
2-ethyltetrazole	—	2.65 (15)	—
1,5-dimethyltetrazole	—	5.30 (15)	—
1-cyclohexyl-5-methyltetrazole	—	6.00 (16)	—
1,5-trimethylenetetrazole (IV)	—	5.88 (g)	—
1,5-pentamethylenetetrazole	—	6.14 (16)	—
1 <i>H</i> -5-(<i>p</i> -tolyl)tetrazole \rightleftharpoons 2 <i>H</i> -5-(<i>p</i> -tolyl)tetrazole (I)	—	—	4.99 (g)
1-methyl-5-phenyltetrazole	—	5.70 (15)	—
1-methyl-5-(<i>p</i> -tolyl)tetrazole (II)	—	6.03 (g)	6.18 (g)
1-methyl-5-(<i>p</i> -nitrophenyl)tetrazole	—	3.87 (17)	—
2-methyl-5-(<i>p</i> -tolyl)tetrazole (III)	—	2.41 (g)	2.43 (g)

(a) See Figure 1. (b) For *C*-deuteriotetrazole and *N*-deuteriotetrazole, respectively (12). (c) Refers to 2*H*-tetrazole (12). (d) By microwave spectroscopy. (e) By Debye refractivity method at 25.0° and for $E^P + A^P = R_D$, unless otherwise specified. (f) For $E^P + A^P = 1.15 R_D$. (g) At 30.0° and for $E^P + A^P = R_D$; uncertainty given in Table II.

Table II
Physical Data from Experimental Dipole Moment Determinations (a)

Compound No. (b)	Solvent	w max	α_0	$-\beta$	$P_2 \infty$	R_D	μ (Debye)
I	dioxan	0.003	17.45 (c)	0.170	544	44.3	4.99 \pm 0.05
II	benzene	0.016	22.30	0.326	780	49.0	6.03 \pm 0.01
II	dioxan	0.020	26.90	0.152	818	49.0	6.18 \pm 0.02
III	benzene	0.017	3.66	0.282	166	49.2	2.41 \pm 0.02
III	dioxan	0.008	4.32	0.109	168	49.2	2.43 \pm 0.03
IV	benzene	0.020	33.30	0.350	723	27.0	5.88 \pm 0.04

(a) At 30.0° in the specified solvent. (b) Name of the compound is given Table I. (c) $\alpha = 17.45 + 725 w$, from ϵ -values on 30 solutions.

of 1*H*-tetrazole and 1-methyltetrazole or 1-ethyltetrazole are close to each other, while those of 2*H*-tetrazole and 2-ethyltetrazole are of the same order of magnitude (Table I).

b.

Direct calculation by using an additivity vector scheme of the dipole moments of the 1*H*- and 2*H*-tautomers is made difficult by interaction of the mesomeric moments which, therefore, cannot be equated to the normal values (m) in more simple compounds. The (Ph-C=Y) mesomeric moment in benzylidene-*N*-methylamine should be somewhat lower than that [$m = 0.4$ D (18)] in acetophenone, since the (Me₂N...C=Y) interaction moments, respectively, are 1.0 (19) and 1.2 D in *p*-dimethylamino-benzylidene-*N*-methylamine and *p*-dimethylaminoacetophenone, the dipole moments of which in benzene are 3.04 (19) and 5.09 D (20) respectively. The (N-Y=Z) meso-

meric moments in 1,5-diazabicyclo[4.3.0]non-5-ene, 2-ethyl-1,2,3-triazoline and formaldehyde dimethylhydrazone are 1.7, 1.9 and 2.1 D (this latter value was recalculated, assuming all nitrogen atoms as sp² hybridized), respectively (21). However, it appears that in the

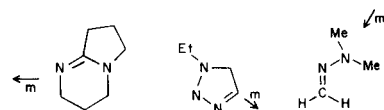


Figure 2

The Mesomeric Moments in 1,5-Diazabicyclo[4.3.0]non-5-ene, 2-Ethyl-1,2,3-triazoline and Formaldehyde Dimethylhydrazone

1*H*-tautomer of tetrazole, the (N-C=N) and (N-N=N) mesomeric moments are approximately additive, and the resultant moment acts almost in the same direction as the

primary moment, which can be obtained from $\mu(\text{H}_2\text{C}=\text{N}) = 1.8 \text{ D}$ (22), $\mu(\text{Me}-\text{N}) = 0.86 \text{ D}$ and $\mu(\text{H}-\text{N}) = 1.25 \text{ D}$. In the $2H$ -tautomer, the $(\text{N}-\text{N}=\text{C})$ and $(\text{N}-\text{N}=\text{N})$ mesomeric moments act in nearly opposite directions, but the resultant moment outweighs the primary moment, so that the dipole moment of the tetrazole $2H$ -tautomer is situated inside the $\text{H}-\text{C}_5-\text{N}_4=\text{N}_3$ half-plane and acts at *ca.* 30° to the $\text{N}-\text{H}$ bond axis (see Figure 1). This observation can explain the large difference between the dipole moments of 1-ethyltetrazole and 2-ethyltetrazole, and 1-methyl-5-(*p*-tolyl)tetrazole (II) and 2-methyl-5-(*p*-tolyl)tetrazole (III), which are all given in Table I.

c.

Due to the weakly acidic character of tetrazoles (25), both $1H$ -5-(*p*-tolyl)tetrazole and $2H$ -5-(*p*-tolyl)tetrazole are likely to give hydrogen-bonded complexes with dioxane, the dipole moments of which can be taken as equal to those of the tautomeric monomeric species in dioxane (26). The dipole moments of the complexes between dioxane and mesomeric HN -containing compounds contain an additional $\Delta\mu$ -term, of *ca.* 0.3 D (27), which is generally [but not always (26)] approximately directed along the acidic $\text{H}-\text{N}$ bond axis. For the $1H$ - and $2H$ -tetrazole cases, the relevant $\Delta\mu$ vector acts approximately [within *ca.* 30° (24)] in the direction of the dipole moment of the particular tautomer. However, such a correction should not be made on the dipole moments of 1-methyl-5-(*p*-tolyl)tetrazole and 2-methyl-5-(*p*-tolyl)tetrazole because, due to increase in the (*N*-residue) mesomeric moment, the dipole moments of mesomeric MeN -containing compounds in benzene are 0.2 - 0.3 D higher than those in the same medium of the corresponding HN -containing derivatives (27).

d.

It has been shown that interannular conjugation is present in non-hindered $1H$ -5-(*p*-tolyl)tetrazole, but absent for obvious sterical reasons in 1-methyl-5-(*p*-tolyl)tetrazole (9). As a consequence, equating $\mu(1H)$ to $\mu(1\text{Me})$ is less satisfactory than equating $\mu(2H)$ to $\mu(2\text{Me})$. However, this problem can be dealt as follows. In planar $1H$ -5-(*p*-tolyl)tetrazole, competition between mesomeric effects in the $(\text{N}-\text{C}=\text{N})$ and $(\text{Ph}-\text{C}=\text{N})$ groups tends to diminish much more $m(\text{Ph}-\text{C}=\text{N})$ than $m(\text{N}-\text{C}=\text{N})$, since the latter is much higher in magnitude: compare the m 's for 1,5-diazabicyclo[4.3.0]non-5-ene and benzylidene-*N*-methylamine given above. In addition the dipole moments of fully conjugated acetophenone and nonconjugated methyl mesityl ketone differ little, being 3.05 and 2.81 D , respectively (30). It then follows that a vector of 0.3 D at the very most should be added to the gross moment of 1-methyl-5-(*p*-tolyl)tetrazole acting at 40° to the $\text{Ph}-\text{C}$ bond axis (31), to represent that (unknown) of the $1H$ -5-(*p*-tolyl)tetrazole tautomer.

With these sufficiently justified assumptions, for 5-(*p*-tolyl)tetrazole $\mu(1H)$ can be equated to $\mu(1\text{Me}) = 6.03 \pm 0.01 \text{ D}$ or, better, to $6.25 \pm 0.01 \text{ D}$, to account for interannular conjugation; $\mu(2H)$ can be equated to $\mu(2\text{Me}) = 2.41 \pm 0.02 \text{ D}$. Accordingly, from the dipole moment of 5-(*p*-tolyl)tetrazole ($4.99 \pm 0.05 \text{ D}$) in dioxane at 30.0° , it follows that the compound, a very dilute dioxane solute (weight fraction inferior to 0.003) is a mixture of $1H$ -5-(*p*-tolyl)tetrazole (62 ± 2 or, better, $57 \pm 2\%$) and $2H$ -5-(*p*-tolyl)tetrazole (38 ∓ 2 , or $43 \mp 2\%$), whence $(1H)/(2H) = (60 \pm 10)/(40 \pm 10)$. This result cannot be compared directly to the tautomer percent $(1H)/(2H)$ ratio ($89/11$) determined for 5-(*p*-tolyl)tetrazole in DMSO -water ($83:17 \text{ v/v}$) by ^{13}C nmr spectroscopy (9), since the latter referred to hydrogen-bonded complexes of $1H$ - and $2H$ -tautomers with strongly polar dimethylsulphoxide [$\mu = 3.9 \text{ D}$ in benzene (28)] or highly iso-associated water [$\mu = 1.84 \text{ D}$ for monomeric water (28)], the dipole moments of which cannot be easily calculated. Further, the solvent reaction-field stabilisation of one tautomer relative to the other markedly depends on the dielectric permittivity of the medium, such that, as observed, increasing it [(DMSO -water) ~ 55 against ϵ (dioxane) = 2.2] results in an increase of the more polar $1H$ -tautomer. However it is interesting that the dipole moment results do agree with the ^{13}C nmr data in suggesting that the $1H$ tautomer of this 5-aryltetrazole is the major form, since it has generally been assumed (erroneously) in the literature that 5-aryltetrazoles exist predominantly as $2H$ -forms.

The fact that, for 5-(*p*-tolyl)tetrazole in dioxane, the $1H$ -tautomer population ($60 \pm 10\%$) is much lower than for unsubstituted tetrazole in the same medium (*ca.* 90%) (14,33), is probably due to interannular conjugation which stabilises the $2H$ -tautomer; the *p*-tolyl group conjugates with two double bonds ($\text{C}=\text{N}$ and $\text{N}=\text{N}$) in the $2H$ -tautomer, and with one conjugated group ($\text{C}=\text{N}-\text{N}=\text{N}$) in the $1H$ -tautomer. Further, hydrogen bonding with dioxane should be somewhat obstructed in the $1H$ -tautomer by the presence of the voluminous *p*-tolyl group, making the dioxane stabilisation weaker than for the $2H$ -tautomer.

Interestingly, normal tetrazole in the gaseous phase exists as the $2H$ -tautomer, while tetrazole in dioxane solution exists mainly in the tautomeric $1H$ -form. For uncomplexed species, which still remain as such in dioxane, this can be due to the solvent reaction-field stabilisation which tends to favour the more polar form; 2-formylfuran exists as (*o,o*)-*trans* in the gaseous phase (34), but as a mixture of (*o,o*)-*cis* and (*o,o*)-*trans* conformers (63 and 37% , respectively) in perdeuteriated dioxane [ϵ close to 2.0 (35)]. Regarding the much more abundant dioxane complexed species, the solvent reaction-field stabilisation also plays a role.

EXPERIMENTAL

Cryoscopic benzene from Prolabo (Paris), and dioxane from Eastman

Kodak (Rochester, USA), were purified and dried as indicated (36); at 30.0°, $d_4 = 0.8686$ and 1.0332 , $\epsilon = 2.2642$ (assumed) and 2.2054 , respectively. 5-(*p*-Tolyl)tetrazole (I), 1-methyl-5-(*p*-tolyl)tetrazole (II) and 2-methyl-5-(*p*-tolyl)tetrazole (III) were prepared by Butler and McEvoy (9), by using literature methods (7), and have previously been examined by ^1H and ^{13}C nmr spectroscopy (9).

Compound I.

This compound formed white crystals, m.p. 252°.

Anal. Calcd. for $\text{C}_9\text{H}_8\text{N}_4$: C, 60.0; H, 5.0; N, 35.0. Found: C, 60.2; H, 5.05; N, 34.7.

Compound II.

This compound formed white crystals, m.p. 117-118°.

Anal. Calcd. for $\text{C}_9\text{H}_{10}\text{N}_4$: C, 62.1; H, 5.7; N, 32.2. Found: C, 62.3; H, 5.6; N, 32.0.

Compound III.

This compound formed white crystals, m.p. 108-109°.

Anal. Calcd. for $\text{C}_9\text{H}_{10}\text{N}_4$: C, 62.1; H, 5.7; N, 32.2. Found: C, 61.9; H, 5.8; N, 32.4.

1,5-Trimethylenetetrazole (IV).

This compound was prepared by Étienne and Corrêia (37) and formed white crystals, m.p. 110°.

Anal. Calcd. for $\text{C}_6\text{H}_8\text{N}_4$: C, 43.6; H, 5.5; N, 5.8. Found: C, 43.7; H, 5.6; N, 50.6.

The electric dipole moments were measured in benzene and/or dioxane at $30.0 \pm 0.05^\circ$ by using the well-known refractivity method. The total polarization of the solute, extrapolated to infinite dilution, was calculated from the experimental ratios (38) where w is the weight

$$\alpha_w = \lim_{w \rightarrow 0} \left(\frac{\epsilon - \epsilon_1}{w} \right) \text{ and } \beta = \frac{\Sigma(v - v_1)}{\Sigma w}$$

fraction of the solute (known with five decimal points), ϵ (determined with four decimal points) and v (measured with five decimal points) are, respectively, the dielectric permittivity and specific volume of the solutions; subscript one refers to the pure solvent as used, *i.e.* made up in the same way as the solutions. The α_w -value has been determined by least-squares analysis of the $\epsilon(w)$ polynomial function, which was found to be quadratic for compound I in dioxane, and linear for compounds II, III and IV in both benzene and dioxane. The distortion polarization of the solute ($E^P + A^P$) was assumed to equal the molecular refraction R_D , determined on solutions.

The dielectric permittivities of the solutions, referred to that of benzene, were measured with a W. T. W. Dipolmeter DM 01 (from Weillheim Oberbayern, West Germany), by using a thermostatted DFL 2 cell adequately modified (39). The specific volumes were accurately measured with a Digital Microdensimeter DMA 02C (from Anton Paar, KG., Graz, Austria), and the refraction indices with a VEB Carl Zeiss interferometer (from Jena, D.D.R.) (25,40).

For each solute examined, the values of w_{max} (reported with only three decimal points), α_w , β (in ml. g^{-1}), $P_{2\infty}^D$ and R_D (both in ml. mole $^{-1}$) and μ (in Debye units) are listed in Table II.

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