664. *The Electric Dipole Moments of Some Dihydrotetrazines and Related Compounds.*

By P. G. Edgerley and L. E. Sutton.

From electric dipole moment measurements, it has been shown that the compounds prepared by Baker, Ollis, and Poole (preceding paper) are probably the true 1 : 4-diaryl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazines, while that prepared by Ruhemann must have an asymmetric, and therefore a different structure.

By considering the moments of the *N*-phenyl-anilinotriazoles, it has been shown that the compound obtained by alkaline rearrangement of 1 : 4-dihydro-1 : 4-diphenyl-1 : 2 : 4 : 5-tetrazine can only be derived from 1-phenyl-1 : 2 : 4-triazole if, as is probable, it is an *N*-phenyl-anilinotriazole.

In order to distinguish between two compounds, both of which were believed to be 1 : 4-dihydro-1 : 4-diphenyl-1 : 2 : 4 : 5-tetrazine, we measured their dipole moments in benzene solution at the request of Prof. W. Baker. The results led to measurement of some further compounds of this type.

Experimental.

All the compounds were supplied by Prof. W. Baker, Dr. W. D. Ollis, and Dr. V. D. Poole. The methods by which they were prepared are described in the preceding paper.

Solvent (benzene) purification and measurements were carried out in the manner described by Everard and Sutton (*J.*, 1949, 2312). The refractive indices of the solutions were determined on a Pulfrich refractometer. The calculations of the polarisations were performed in the way described by Everard, Hill, and Sutton (*Trans. Faraday Soc.*, 1950, **46**, 417). The symbol convention is also the same as in that paper.

1 : 4-*Dihydro*-1 : 4-*diphenyl*-1 : 2 : 4 : 5-*tetrazine* (I).

ω.	ε.	v.	Δn.
0·000476	2·2730	1·14524	—
0·002459	2·2741	1·14434	—
0·003498	2·2754	1·14444	—
0·004562	2·2757	1·14361	—
0·004991	—	—	0·00068

1 : 4-*Di*-p-*chlorophenyl*-1 : 4-*dihydro*-1 : 2 : 4 : 5-*tetrazine* (II).

ω.	ε.	v.	Δn.
0·002209	2·2733	1·14416	—
0·002891	2·2736	1·14394	—
0·006699	2·2756	1·14198	—
0·008870	2·2762	1·14138	—
0·014329	—	—	0·00189

1 : 4-*Dihydro*-1 : 4-*di*-p-*tolyl*-1 : 2 : 4 : 5-*tetrazine* (III).

0·001274	2·2734	1·14492	—
0·002672	2·2742	1·14447	0·00031
0·004126	2·2749	1·14416	0·00047
0·008968	2·2777	1·14269	0·00104

Ruhemann's compound, $C_{14}H_{12}N_4$ (IV).

0·001385	2·2759	1·14459	—
0·003482	2·2816	1·14380	—
0·004254	2·2833	1·14359	—
0·006425	2·2879	1·14280	—
0·007634	—	—	0·00095

Alkaline rearrangement product of (I) (*probably* 3-*anilino*-1-*phenyl*-1 : 2 : 4-*triazole*) (V).

0·002310	2·2865	1·14595	—
0·004015	2·2970	1·14529	—
0·006363	2·3116	1·14442	—
0·008576	2·3242	1·14342	0·00086

The dipole moments of the dihydrotetrazines and some related compounds in benzene solution at 25°.

	α.	ε_1.	β.	v_1.	γ.	${}_{T}P_2$.	${}_{E}P_2$.	μ, D.
(I)	0·69	2·2727	0·36	1·14534	0·14	85·9	72·9	0·8
(II)	0·53	2·2721	0·49	1·14513	0·13	94·3	86·1	0·65
(III)	0·56	2·2727	0·29	1·14529	0·12	95·2	84·0	0·75
(IV)	2·41	2·2728	0·35	1·14506	0·12	162·8	71·7	2·11
(V)	6·03	2·2727	0·40	1·14477	0·10	320·6	80·6	3·54

The dipole moments of (I), (II), and (III) are quoted to the nearest 0·05 D., which is the probable error in μ owing to the practical limitations of the experimental technique. The moments of compounds (IV) and (V) are subject to an error of $\pm 0{\cdot}02$ D.

As usual with compounds of low dipole moments (I, II, and III) it is not possible to obtain very precise values owing to the uncertainty about atom polarisation. The moments quoted above were obtained by making the assumption that ${}_{E}P_2 + {}_{A}P_2$ is equal to the molar refraction for the Na_D line, $[R]_D$. The following table, however, shows the polarisations of (I), (II), and (III) on the assumption that ${}_{A}P$ is 12% of $[R]_D$.

	$[R]_D$.	${}_{O}P'_2$.	μ', D.
1 : 4-Dihydro-1 : 4-diphenyl-1 : 2 : 4 : 5-tetrazine (I)	81·4	4·4	0·4
1 : 4-Di-*p*-chlorophenyl-1 : 4-dihydro-1 : 2 : 4 : 5-tetrazine (II)	96·4	—	0·0
1 : 4-Dihydro-1 : 4-di-*p*-tolyl-1 : 2 : 4 : 5-tetrazine (III)	94·1	1·0	0·2

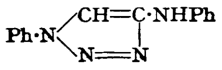
DISCUSSION.

From the moments of the compounds prepared by Baker *et al.* (see above) and that of Ruhemann's compound, it is reasonably certain that the former are the true dihydrotetrazines but that Ruhemann's compound must possess another structure.

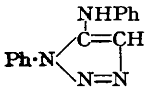
Although, by making the assumptions that we normally do with regard to atom polarisation, the compounds appear to have small moments, it can be seen from the foregoing table that an atom polarisation of about 12% of ${}_{E}P$ is sufficient to reduce the moments of all three dihydrotetrazines effectively to zero. *trans*-Azobenzene, if we assume it to be symmetrical, has an atom polarisation of 8—10% of ${}_{E}P$ (Hartley and Le Fèvre, *J.*, 1939, 531; Bergmann, Engel, and Sandor, *Ber.*, 1930, **63**, *B*, 2572). It is therefore probable, but not certain, that the moments of the dihydrotetrazines are zero. If this were so, it would be a possible conclusion, though not a necessary one, that the ring system is completely flat, as Baker *et al.* have suggested on the evidence of their visible and ultra-violet absorption spectra. If there is a small moment, this could be due to the dihydro-ring system being not quite flat, but slightly buckled, the phenyl groups probably remaining roughly anti-parallel to each other. With the present measurements a definite choice between these possibilities cannot be made.

Without further analysis, all that can be said of the isomers of dihydrodiphenyltetrazine (Ruhemann's compound and the alkaline rearrangement product V), is that they are asymmetric. By making reasonable assumptions it is, however, possible to reach a more definite conclusion.

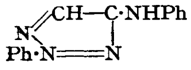
Baker, Ollis, and Poole (*loc. cit.*) conclude that (V) is an *N*-phenyl-anilinotriazole. Now there are six possible *N*-phenyl-anilinotriazoles, as shown below: under each is given the moment of the parent *N*-phenyltriazole (Jensen and Friediger, *Kgl. Danske Mat.-fys. Metteleser*, 1943, **20**, 20).



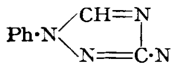
4-Anilino-1-phenyl- 1 : 2 : 3-triazole.
Parent moment: 4·08 D.



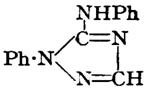
5-Anilino-1-phenyl- 1 : 2 : 3-trizaole.
4·08 D.



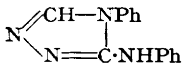
4-Anilino-2-phenyl- 1 : 2 : 3-triazole.
0·97 D.



3-Anilino-1-phenyl-
1 : 2 : 4-triazole.
Parent moment : 2·88 D.

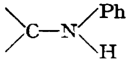


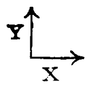
5-Anilino-1-phenyl-
1 : 2 : 4-triazole.
2·88 D.



3-Anilino-4-phenyl-
1 : 2 : 4-triazole.
5·63 D.

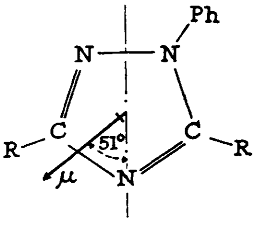
Next, it may be shown that the effect of anilino-substitution into an *N*-phenyltriazole must be to increase the moment. The anilino-group is bent; but the mean moment is the same whether the group rotates freely about the bond joining it to the triazole ring or assumes equally two positions in which it is held coplanar with the triazole ring by π-bonding between the two. If μ_1 is the fixed moment and μ_2 the rotating one then, whatever the angle between the former and the axis of rotation of the latter, the mean moment is $\sqrt{\mu_1^2 + \mu_2^2}$. By resolving the moment of the anilino-group into a non-rotating component μ_X (along the C–N axis) and a rotating one μ_Y (= μ_2) perpendicular to this, the mean moment may easily be evaluated, because μ_1 is the vector resultant of μ_X and the moment of the parent compound :





Using the best available values for the C–N, Ph–N, and N–H bond moments (cf. Hill and Sutton, *J.*, 1949, 746; Everard and Sutton, *ibid.*, p. 2320), we find that the σ-bond component along X is from 0·0 to 0·3 D. *out of* the hetero-ring. There is also a possible π-bond moment which may be taken as between 0·0 and 0·5 D. *into* the ring. The σ-bond component μ_Y (= μ_2) is found to be about 2 D. μ_X may augment the parent moment, in which event the mean total moment is increased both from this cause and from the effect of μ_2; but even if μ_X opposes the parent moment, its effect, since it is small, will be outweighed by that of μ_2 which always increases the moment. In general, therefore, substitution by the anilino-group increases the moment, though by an amount which depends upon the magnitude and direction of the parent moment. The increase is less the greater the parent moment, and when the latter is 1 D., the maximum increase due both to μ_X and to μ_2 is about 1·7 D.

From the moments of the parent compounds, it is immediately obvious that compound (V), of moment 3·54, cannot be derived from 1-phenyl-1 : 2 : 3-triazole (two isomers) or 4-phenyl-1 : 2 : 4-triazole; two of these possibilities had, indeed, already been eliminated because 5-anilino-1-phenyl-1 : 2 : 3-triazole and 3-anilino-4-phenyl-1 : 2 : 4-triazole are already known (Dimroth, *Annalen*, 1908, **364**, 225; Busch, *Ber.*, 1900, **33**, 1067). It is also obvious that (V) cannot be derived from 2-phenyl-1 : 2 : 3-triazole which has too small a moment to be increased to 3·54 by anilino-substitution. The remaining possibilities are, therefore, 3- or 5-anilino-1-phenyl-1 : 2 : 4-triazole. Between these, from dipole evidence alone, we cannot choose : Baker, Ollis, and Poole (*loc. cit.*), from considerations of probable reaction mechanism, have chosen the former. We may add that if Ruhemann's compound should prove to be an *N*-phenyl-anilino-triazole we should expect it to be the 4-anilino-2-phenyl-1 : 2 : 3-triazole because its moment is 2·1 D.



It may be shown that either 3- or 5-anilino-1-phenyl-1 : 2 : 4-triazole should have a moment very close to that observed for compound (V). Taking the direction of the parent moment to be that calculated by Orgel, Cottrell, Dick, and Sutton (to be published) (see figure), and assuming that the substitution moment consists of μ_X = 0·3 out of the ring *or* 0·5 into it, and that $\mu_Y = \mu_2 = 2$ (see above), we find that the moment of the former compound is 3·15—3·75 D., and that of the latter is 3·4—3·75 D., the arithmetical means being 3·45 and 3·55.

The moment of 4-anilino-2-phenyl-1 : 2 : 3-triazole, calculated similarly, should be 2·1—2·3 D.

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