Tetrahedron Vol. 33, pp 2583 to 2586. Pergamon Press 1977. Printed in Great Britain

ANALYSIS OF THE DIPOLE MOMENTS OF SOME POSSIBLE THIOURONIUM AND GUANIDINIUM FLUORENYLIDES

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(*Received in UK* 16 *February* 1977; *Accepted for publication* 19 *April* 1977)

Abstract—The dipole moments of "thiouronium fluorenylide", "N,N'-diphenylthiouronium fluorenylide", and "N,N'-diphenylguanidinium fluorenylide" are analysed, confirming that the thiourea derivatives exist largely, and the guanidine derivative entirely, as prototropic fluorenyl-isothioureas or diphenylguanidine respectively.

A recent publication[1] has described the preparation and properties of some thiouronium and guanidinium fluorenylides and cyclopentadienylides, and the properties of the thiourea derivatives (**1**) and the guanidine derivative (**2**) suggest that the former exist largely and the latter entirely in the prototropic fluorenylisothiourea (**1B**) and fluorenylguanidine (**2B**) forms respectively. We now make an analysis of the dipole moments of **1** (R = H and Ph) and of **2**, which are in accord with these formulations.

The dipole moments of the thiourea derivatives and of some related sulphonium ylides are listed in Table 1. The thiourea derivatives have markedly smaller dipole moments than the sulphonium ylides.

The ylide tautomeric forms **1A** of the thiouronium ylides are hybrids of the covalent structures **1A**(1) and the dipolar structures **1A**(2). They should therefore exhibit dipole moments markedly higher than those calculated for the covalent structure **1A**(1). The latter can be estimated from the dipole moments of dimethylsulphonium fluorenylide (6.2D) and the pertinent thioureas, on the basis of the following assumptions:

(i) By analogy with triphenylphosphonium fluorenylide, which has a dipole moment (7.09D)[4] whose sign is clearly indicated by the dipole moments of triphenyl- and tri - (*p* - chlorophenyl) - phosphonium 2,7-dibromofluorenylides (6.73 and 4.98D),[5] the dipole moment of dimethylsulphonium fluorenylide is directed from the S atom towards the ring.

Table 1. Dipole moments of sulphonium ylides

	μ(D)
Dimethylsulphonium fluorenylide[2]	6.2[a]
Methylphenylsulphonium tetraphenylcyclopentadienylide[3]	6.69[a,c]
Diphenylsulphonium tetraphenylcyclopentadienylide[3]	6.90[a,c]
"Thiouronium fluorenylide" (I, R = H)	2.15[b]
"N,N'-Diphenylthiouronium fluorenylide" (I, R = Ph)	2.35[a]

[a] In benzene solution.
[b] In dioxan solution.
[c] The first two lines in the table in ref. (3) should read as given here.

(ii) The dipole moment of the nearly trigonal $Me\ddot{S}Me$ group in dimethylsulphonium fluorenylide is equal to $[\mu(Me_2\ddot{S}:) - \mu_h(S, 100°C)]/2 \cos 50°) = 1.13–2.01 = -0.88D$, where μ_h (S, 100°) stands for the hybridisation moment of the sulphur atom if S = 100°.[6]

(iii) The dipole moment of thiourea in dioxan is 5.07D,[7] and that of N,N'-diphenylthiourea, which exists *cis-trans*,[8] is 4.85D (present work) and they each contain a hydridisation moment of either 2.66 or nil according to whether the sulphur atom is hybridised sp^2 or[9] not hybridised.

Based on these assumptions one readily calculates μ(**1A**(1), R = H) to be 9.49D or 12.15D and μ(**1A**(1), R = Ph) to be 9.27D or 11.39D by writing $\mu(\mathbf{1A}(1)) = 6.2 + (5.07\ (R = H)\ \text{or}\ 4.85\ (R = Ph)) + [(0.88 - 2.66)$ or $(0.88 - 0.0)]$. Each of these figures is very much *higher* than the experimental dipole moments μ(**1A**(1), R = H) = 2.06D (in dioxan) and μ(**1A**(1), R = Ph) = 2.35D (in benzene). (The dipole moment of N,N'-diphenylthiourea cannot be determined in benzene, but it probably does not differ significantly from that in dioxan since the values for thiourea in benzene and dioxan are, respectively, 5.0 and 5.07D[7]).

An attempt has been made to calculate the dipole moments of the less hindered conformers (**3**) of the non-ylide form (**1B**), both of which have the C(9)–H and S–Cα bonds staggered, from the dipole moments of fluorene (0.58D, bisecting the SCH angle and directed from C(Fl) towards the ring), dimethyl sulphide (1.45D),[10] and 2 -ethyl - 2 - thiazoline (0.95D), whence the (S–C=N) mesomeric moment (0.9D) is deduced,[11] and of the pertinent formamidines contained in **1B** ≡ **3** (R = H or Ph). In this computation the following assumptions have been made:

(i) In formamidine, N,N - dimethyl - N' - phenylformamidine and N,N'-diphenylformamidine, and also in structures **3A** and **3B**, the N'–R' and C–N bonds are *trans* to each other. By analogy with formanilide,[12] N,N'-diphenylformamidine is supposed to exist as a nearly equal mixture of *cisoid* (A) and *transoid* (B) conformers (**4**), but, like acetanilide[13] (which exists in an endo form), the N,N'-diphenylformamidine moiety in 3 (R, R' = Ph) is assumed to be *cis*.

(ii) Due to N'-inductive effect in phenyl, the Ph–N' group moment is taken to equal μ(Mesityl-N) = 1.24D (ref. 14), a value close to that for the H–N (sp^3) bond moment (1.25D) derived from the electric moment of ammonia[10] (1.41D in benzene). Comparison of the dipole moments in benzene of acetanilide[15] (3.60D, acting at 75 ± 2° to the N–Ph bond axis) and of N-methylacetamide[16] in the *cisoid* form[17] (3.80D) affords μ(Ph–N) − μ(Me–N) = +0.64. [Comparison of such a μ(Ph–N) − μ(Me–N) difference with μ(Ph–N) − μ(Me–N) = −1.66D in the case of N,N-dimethylaniline[14] shows that the severe competition between the (N–C=O) and (N–Ph) mesomeric effects in acetanilide suppresses the smaller (N–Ph) effect. The rotational barriers for the dimethylamino groups in N,N-dimethylformamide[18] and N,N-dimethylaniline[17] are, respectively, 20.5 and 5.1 kcal mole^{-1}]. The effective H–N bond moment in formamidine and in thiouronium fluorenylides (as the prototropic forms 3) in dioxan as solvent is μ(dioxan...H–N) = μ(H–N) + $\Delta\mu$ = μ(H–N) + 0.3, taking $\Delta\mu$ as equal to the vectorial difference (along the H–N bond axis) between the moments of acetanilide[15] in dioxan and in benzene (3.88 and 3.60D).

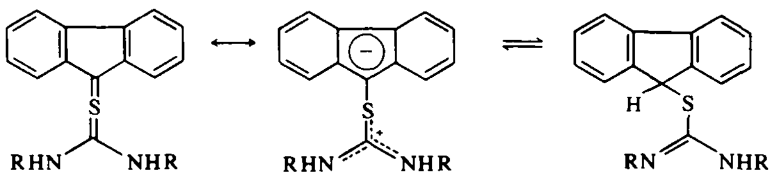
(iii) The directions of the dipole moments of the N,N'-diphenylformamidine conformers (**4A,B**), which are both assumed to equal the dipole moment of the compound[20] (2.20, in dioxan) since μ(H–N) − μ(Me–N) = 0.39D, and, consequently, μ(dioxan ... H–N) ~ μ(Ph–N), are derived from the dipole moment of N,N-dimethyl-N'-phenylformamidine[21] in cyclohexane (a 2.92D vector acting at 37.5° to the N'-Ph bond axis), by adequately changing relevant bond moments and by reducing (by 1.0D) the (N–C=N') mesomeric moment; a decrease of 0.7D in the (N–C=O) mesomeric moment is likely to occur on going from N,N-dimethylacetamide to acetanilide. (For the determination of the mesomeric moments of amides and amidines, see refs 22, 23). The dipole moment of formamidine in dioxan is readily deduced from that of N,N'-diphenylformamidine.

Calculations on these bases can only give, of course, approximate values (within ±0.1) for the dipole moments of the A and B conformers of 3 (R = H) in dioxan and 3 (R = Ph) in benzene, as follows:

$$3,\ R = H:\ \mu(A) = 3.35D,\ \mu(B) = 1.7D$$
$$3,\ R = Ph:\ \mu(A) = 3.3D,\ \mu(B) = 1.65D.$$

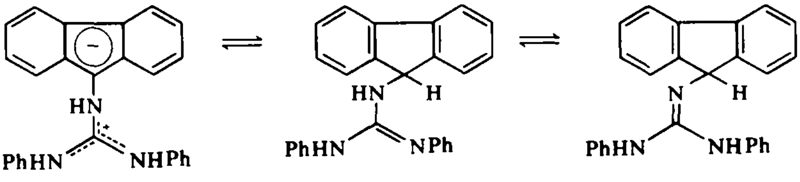
Nearly equal values are obtained by assuming $\Delta\mu$ = μ(dioxan) − μ(benzene) as directed along the (N–C=X) mesomeric moment (see "Added in Proof").

Comparison of these values with the experimental figures (2.06 and 2.35D) thus shows that the potentially tautomerisable so-called thiouronium and N,N'-diphenylthiouronium fluorenylides in fact exist predominantly in the non-ylidic forms **1B** = **3**, mainly in the

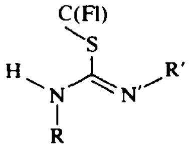


(1) (2)

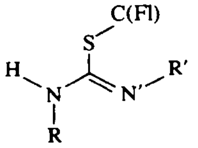
1A **1B**



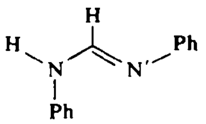
2A **2B** **2C**



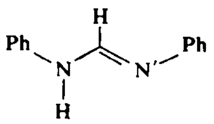
3A



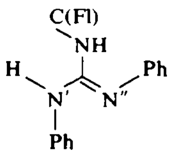
3B



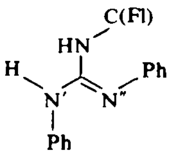
4A



4B



5A



5B

Table 2. Dipole moment determinations

Compound	Solvent	w_{max}	α	$-\beta$	$P_{2\infty}$	$R_{2\infty}$	μ(D) (at 30°)
N,N′-Diphenylthiourea	Dioxan	0.005	13.0	0.184	544	72	4.85[a]
N,N′-Diphenylguanidine	Benzene	0.008	5.23	0.270	265	66	3.14[b]
"Thiouronium fluorenylide" (**1**, R = H)	Dioxan	0.004	2.9	0.205	169	83.5	2.06
"N,N′-Diphenylthiouronium fluorenylide" (**1**, R = Ph)	Benzene	0.012	2.0	0.317	246	135	2.35
"N,N′-Diphenylguanidinium fluorenylide" (**2**)	Benzene	0.006	2.62	0.324	279	126.5	2.75

[a] Ref. 10 gives 4.85, 4.9 and 5.05D.

[b] Ref. 28 gives μ = 2.19D; diphenylguanidine (isomer and solvent not specified in *Chem. Abstr.*) μ = 2.79D.[29]

less-hindered conformation **3B**. In this conformation planarity of the HRN–C=N′ group is more easily achieved than in conformer **3A**, thus permitting the molecule to benefit from the (N–C=N′) conjugation energy, which is high in amidines[24] (E_a = 13.0 kcal mole^{-1} in N,N - dimethyl - N′ - t - butylformamidine[24]).

In the case of the "N,N′-diphenylguanidinium fluorenylide", the dipole moment (2.75D, in benzene) clearly precludes any significant contribution from the ylide structure, whose predicted moment is as high as 18–19D.

Assuming, by analogy with N,N′-diphenylurea, that N,N′-diphenylguanidine exists in the (less-hindered) *cis-trans* form, then the dipole moment of the tautomer (**2C**), which exists in a unique conformation, may be calculated, by using the moments of N,N′-diphenylguanidine (3.14D, present work) and of fluorene, to be 3.6D.

The tautomer (**2B**) can exist in a number of conformations, among which the least hindered are **5A** and **5B**. The dipole moments of these conformers can readily be derived from the moments in benzene of N,N′-diphenylguanidine and of fluorene, by changing the pertinent bond moments. In this way one can obtain values for **5A** = 1.8D and for **5B** = 2.5_5D.

These results may be compared with the observed dipole moment of the compound in benzene, 2.75D, and suggest, therefore, that "N,N′-diphenylguanidinium fluorenylide" exists mainly in the tautomeric form **2B**, and in the conformation **5B**.

Thus the dipole moment measures strongly support the contention[1] that the isothiourea compounds **1** (R = H or Ph) exist largely as the non-ylidic tautomers, and that the guanidine derivative **2** has a completely non-ylidic structure.

EXPERIMENTAL

Dipole moment measurements. The electric moments were measured at 30.0° by the refractivity method. The total polarisation of the solute ($P_{2\infty}$), extrapolated to infinite dilution, was calculated from the ratios:[25]

$$\alpha = \frac{\Sigma(\epsilon - \epsilon_1)}{\Sigma w} \quad \text{and} \quad \beta = \frac{\Sigma(v - v_1)}{\Sigma w}$$

where w is the weight fraction of the solute (inferior to w_{max}), ϵ and v are the dielectric constant and specific volume of the solutions, and subscript 1 refers to the pure solvent used, i.e. prepared in the *same* way as the solutions. The distortion polarisation (${}_{E}P + {}_{A}P$) was assumed to be equal to the molecular refraction of the solution, calculated from

$$\gamma = \Sigma\,(n^2 - n_1^{\,2})/\Sigma\, w \text{ and } \beta \text{ experimental ratios.}$$

The technique for the measurement of the dielectric constants is described in refs 26 and 27. Specific volumes have been determined accurately with a Digital Microdensimeter DMA 02C ("Anton Paar KG", Graz, Austria), and the refraction indices (for sodium D line) with a Bellingham and Stanley differential interferometer.

For each solute, w_{max} (known with 5–6 decimal places, but given only to three), α, β, $P_{2\infty}$, $R_{2\infty}$ and μ (in Debye units) are given in Table 2.

Added in Proof. Such a hypothesis can only explain results found by two of us (H. Lumbroso and C. Liégeois) for ring-closed 2-acylpyrroles, and the fact that the dipole moments of N,N′-ethyleneurea, N,N′-tetramethyleneurea, N,N′-ethylenethiourea, N,N′-trimethylenethiourea and N,N′-tetramethylenethiourea are much greater in dioxan than in benzene [E. J. Lien and W. D. Kumler, *J. Medicin. Chem.* **11**, 214 (1968)].

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