

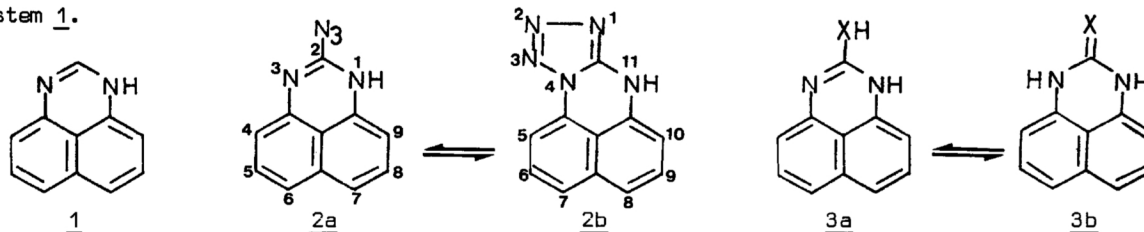
AZIDOAZOMETHINE-TETRAZOLE ISOMERISM IN TETRAZOLO[1,5-a]PERIMIDINE

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The equilibrium between 2-azidoperimidine and tetrazolo[1,5-a]perimidine is strongly shifted towards the latter reflecting the poor aromatic character of the perimidine ring. The title compound is the first example of a new class of condensed tetrazoles.

Perimidine 1 is a very unusual π -rich heteroaromatic substance^{1,2}. As other π -rich heteroaromatics (like imidazole) it possesses a tautomerisable proton^{3a}, but, similarly to the π -deficient ones, it is a six membered ring system. We have studied the position of the azidoazomethine-tetrazole equilibrium for compound 2 as a way to know the aromaticity degree of the 14 π -electron system 1.

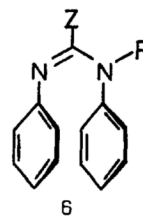
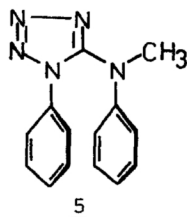
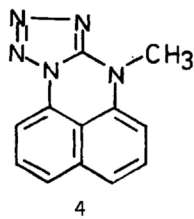


In a previous paper⁴ on azidoazomethine-tetrazole isomerism in thiazole derivatives we made the hypothesis that a rough parallelism exists between azido-tetrazole and prototropic equilibria, i.e. $2a \rightleftharpoons 2b$ and $3a \rightleftharpoons 3b$, both being related to the aromaticity of the parent heterocycle^{5a} (the more aromatic is the compound, the more stable are the isomer 2a and the tautomer 3a). It is known from literature results^{3b} that tautomer 3b, X = NH, is more stable than the corresponding 3a in other aminoazines. If our hypothesis is sound, 2b should be particularly stable.

After an unsuccessful attempt to get 2 from 2-aminoperimidine (3a, X = NH), *via* the diazonium salt with sodium azide, we prepared this compound from 2-chloroperimidine⁶ by reaction with ammonium azide in DMF⁷. The product obtained (mp 240°C, decomp., 70% yield) shows spectroscopic properties (Table I) which are only compatible with tetrazolo[1,5-a]perimidine 2b.

The lack of solubility of 2b in non polar solvents (which favour^{4,8} the azido form) prompted us to prepare the N-methyl derivative 4 (mp 220°C, decomp., 90%), by treating 2b with an equivalent amount of NaH in DMSO to afford the corresponding anion which was then methylated with an excess of CH₃I at room temperature. The position of the N-CH₃ group in compound 4 was determined by the comparison of its ¹³C chemical shifts (Table I) with those of compound 2b. In IR no ν_{as} N₃ band in the range 2100-2200 cm⁻¹ could be detected for the 11-methyl derivative 4 even in CCl₄.

From Linear Free Energy Relationships some authors⁹ have suggested an analogy between perimidine 1 and N,N'-diphenylamidines 6. Because of this we have prepared the 5-(N-methylanilino)-1-phenyltetrazole 5 which behaves as 4 (Table I). Compound 5 was obtained from 5-chloro-1-phenyltetrazole and the lithium derivative of N-methylaniline in anhydrous benzene in quantitative yield, mp 77-78°C. The tetrazole 5 is the ring tautomer corresponding to the azidoazomethine structure 6, R = CH₃, Z = N₃.



Now is possible to come back to our hypothesis of a relationship between aromaticity and ring-chain tautomerism: for a typical π -rich heteroaromatic compound, like imidazole^{5b}, its 2-azido derivative exists as a stable azidoazomethine compound⁸, while for a poor aromatic derivative, like perimidine^{5c}, the tetrazolic form is stable. Anyhow, after a large number of papers devoted to tetrazolo azines⁸ and tetrazolo azoles^{4,8,10}, compounds 2b and 4 are the first examples of a new class of polycyclic tetrazoles.

TABLE I. Spectroscopic properties

Compound	IR (a)	¹ H NMR		¹³ C NMR (f)	MS (12 eV)
<u>2b</u>	KBr DMSO DMF TFAA (b)	DMSO-d ₆ (250 MHz) (c) H ₅ : 7.54; H ₆ : 7.4; H ₇ : 7.4; H ₈ : 7.29 H ₉ : 7.4; H ₁₀ : 6.82; H ₁₁ : 11.8 (broad)		DMSO-d ₆ (20 MHz) 106.0; 107.0; 118.5 124.1; 127.5; 128.8	M ⁺ = 209 (100%) M-N ₂ ⁺ = 181 (35%)
<u>4</u>	KBr DMSO CHCl ₃ CCl ₄ TFAA (b)	DMSO-d ₆ (60 MHz) N-CH ₃ : 3.60 H ₁₀ : 6.93 others: 7.4-7.9	CDCl ₃ (60 MHz) N-CH ₃ : 3.66 H ₁₀ : 6.73 others: 7.2-7.7	DMSO-d ₆ (20 MHz) 105.3; 106.3; 119.2 124.2; 127.6; 128.6	M ⁺ = 223 (100%) M-N ₂ ⁺ = 195 (15%)
<u>5</u>	KBr DMSO CHCl ₃ CCl ₄ TFAA (b)	DMSO-d ₆ (60 MHz) N-CH ₃ : 3.47 (d) : 7.36 (e) : 6.8-7.2	CDCl ₃ (60 MHz) N-CH ₃ : 3.58 (d) : 7.22 (e) : 6.7-7.1	DMSO-d ₆ (20 MHz) 121.8; 124.4; 129.0 129.2	M ⁺ = 252 (100%) M-N ₂ ⁺ = 223 (24%)

(a) Absence of the ν_{as} N₃ band; (b) Freshly prepared solution; (c) Prototropic tautomerism, which is fast in proton NMR time scale for perimidines (J. Elguero, C. Marzin, and M.E. Peek, unpublished results), make 2a "symmetric" (two superimposed ABC systems); (d) Aromatic protons of the N₁-phenyl group; (e) Aromatic protons of the N-methylaniline; (f) Only tertiary carbon atoms.

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(Received September 16, 1977)