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

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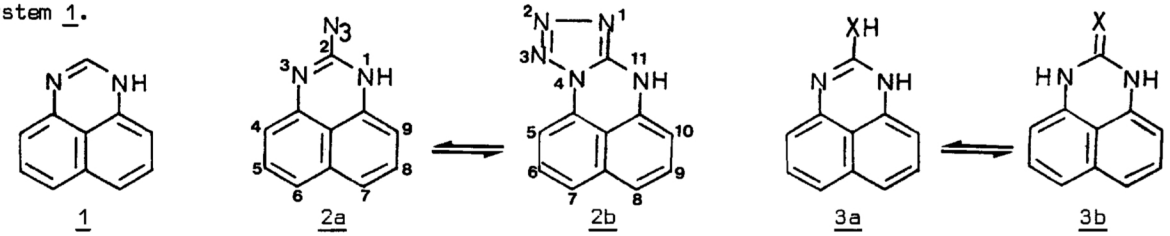
The equilibrium between 2-azidoperimidine and tetrazolo[1,5-*a*]perimidine is strongly shifted towards the latter reflecting the poor aromatic character of the perimidine ring. The title compound is the first example of a new class of condensed tetrazoles.

Perimidine 1 is a very unusual $\pi$-rich heteroaromatic substance[1,2]. As other $\pi$-rich heteroaromatics (like imidazole) it possesses a tautomerisable proton[3a], but, similarly to the $\pi$-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$\pi$-electron system 1.



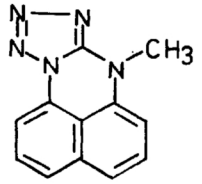
1 2a 2b 3a 3b

In a previous paper[4] 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 unsuccesful attempt to get 2 from 2-aminoperimidine (3a, X = NH), *via* the diazonium salt with sodium azide, we prepared this compound from 2-chloroperimidine[6] by reaction with ammonium azide in DMF[7]. 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 $CH_3I$ at room temperature. The position of the N-$CH_3$ group in compound 4 was determined by the comparison of its $^{13}C$ chemical shifts (Table I) with those of compound 2b. In IR no $\nu_{as}$ $N_3$ band in the range 2100-2200 $cm^{-1}$ could be detected for the 11-methyl derivative 4 even in $CCl_4$.

From Linear Free Energy Relationships some authors[9] 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 = $CH_3$, Z = $N_3$.



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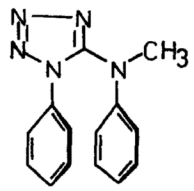

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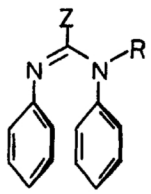

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Now is possible to come back to our hypothesis of a relationship between aromaticity and ring-chain tautomerism: for a typical $\pi$-rich heteroaromatic compound, like imidazole[5b], its 2-azido derivative exists as a stable azidoazomethine compound[8], while for a poor aromatic derivative, like perimidine[5c], the tetrazolic form is stable. Anyhow, after a large number of papers devoted to tetrazolo azines[8] 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) |
|---|---|---|---|---|---|
| 2b | KBr<br>DMSO<br>DMF<br>TFAA (b) | DMSO-$d_6$ (250 MHz) (c)<br>$H_5$: 7.54; $H_6$: 7.4; $H_7$: 7.4; $H_8$: 7.29<br>$H_9$: 7.4; $H_{10}$: 6.82; $H_{11}$: 11.8 (broad) | | DMSO-$d_6$ (20 MHz)<br>106.0; 107.0; 118.5<br>124.1; 127.5; 128.8 | $M^{+\cdot}$ = 209 (100%)<br>$M-N_2^{+\cdot}$ = 181 (35%) |
| 4 | KBr<br>DMSO<br>$CHCl_3$<br>$CCl_4$<br>TFAA (b) | DMSO-$d_6$ (60 MHz)<br>N-$CH_3$: 3.60<br>$H_{10}$: 6.93<br>others: 7.4-7.9 | $CDCl_3$ (60 MHz)<br>N-$CH_3$: 3.66<br>$H_{10}$: 6.73<br>others: 7.2-7.7 | DMSO-$d_6$ (20 MHz)<br>105.3; 106.3; 119.2<br>124.2; 127.6; 128.6 | $M^{+\cdot}$ = 223 (100%)<br>$M-N_2^{+\cdot}$ = 195 (15%) |
| 5 | KBr<br>DMSO<br>$CHCl_3$<br>$CCl_4$<br>TFAA (b) | DMSO-$d_6$ (60 MHz)<br>N-$CH_3$: 3.47<br>(d) : 7.36<br>(e) : 6.8-7.2 | $CDCl_3$ (60 MHz)<br>N-$CH_3$: 3.58<br>(d) : 7.22<br>(e) : 6.7-7.1 | DMSO-$d_6$ (20 MHz)<br>121.8; 124.4; 129.0<br>129.2 | $M^{+\cdot}$ = 252 (100%)<br>$M-N_2^{+\cdot}$ = 223 (24%) |

(a) Absence of the $\nu_{as}$ $N_3$ 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 $N_1$-phenyl group; (e) Aromatic protons of the N-methylaniline; (f) Only tertiary carbon atoms.

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