Tetrahedron Letters Vol. 21, pp 3799 - 3800 0040-4039/80/0922-3799$02.00/0

1,3-DICHLOROMETHINE CYANINE CONDENSATION WITH 1,3-DIMETHYL-4,5-DIAMINO URACIL PRODUCING A NEW SPIRO-HETEROCYCLE[1]

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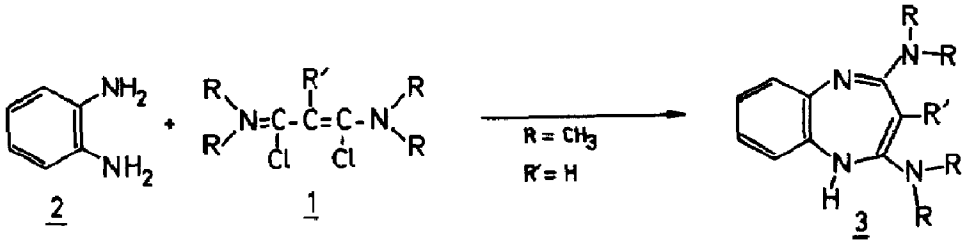
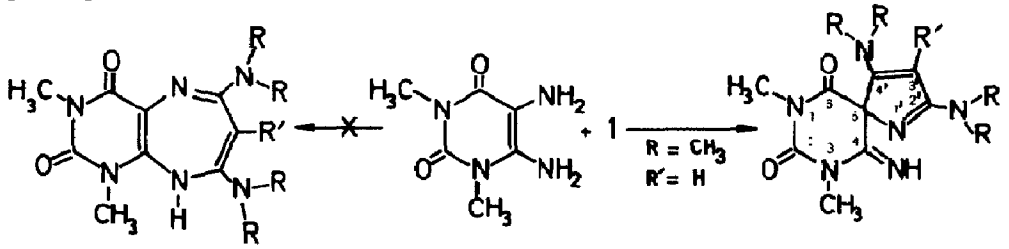
Summary: Trimethinium salts 1 cyclize with 4,5-diaminouracil to give the new spiroheterocyclic systems 6

1,3-Dichloromethine cyanines 1 are easily obtained derivatives of phosgeminium salts and acetamides. 1 lead by heterocyclisation to 5,6 or 7 membered rings derivatives [2,3,4]. In particular, 1,4-benzodiazepines 3 have been formed from 2 and structurally proved by X-ray analysis [5].



2 1 3

While attempting to apply this principle to 1,2-diamino systems of biological importance, the 1,3-dimethyl 4,5-diamino uracil 4 again furnished a condensation product in high yield. Its X-ray analysis, however, proves now the unexpected structure of 1,3-dimethyl-4-imino-5,5-(spiro-2',4'-bis-dimethylamino-pyrrolyl)uracil 6, instead of diazepine 5.



5 4 6

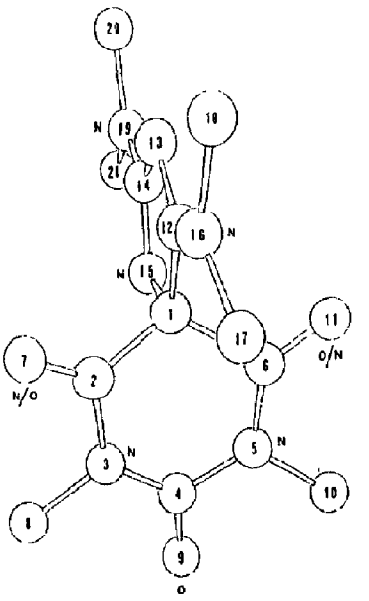
The report of its biological interest for "*In vivo*" reactivation of cholinesterase inhibited by organophosphates [6] has initiated this publication on the synthesis and structure of 6 as part of a series to be reported later.

X-RAY STRUCTURE DETERMINATION

Crystal data : orthorhombic, Fdd2 ; a=34.639(9), b=20.183(6), c=8.508(3) Å ; Z = 16. The structure was solved by MULTAN 77 [7] and refined by XRAY 72 [8] on the basis of 572 reflections with $I > 2.5\sigma(I)$. MoKα radiation (λ = 0.7107 Å). Final 0.08.

ATOMIC COORDINATES

ATOM			
C1	4264 (5)	7763 (9)	6363 (0)
C2	4133 (7)	7723 (11)	8055 (33)
N3	4256 (4)	7118 (7)	8007 (29)
C4	4531 (5)	6711 (10)	8298 (34)
N5	4749 (4)	6888 (7)	6949 (29)
C6	4673 (6)	7405 (11)	5952 (38)
O/N7	3947 (5)	8120 (8)	8717 (30)
C8	4879 (8)	6972 (12)	10388 (35)
C9	4623 (5)	6212 (7)	8961 (31)
C10	5104 (6)	6512 (11)	6615 (35)
O/N11	4838 (4)	7539 (8)	4773 (31)
C12	4265 (5)	8471 (8)	5776 (33)
C13	3971 (5)	8525 (9)	4672 (35)
C14	3806 (5)	7855 (9)	4482 (33)
N15	3959 (4)	7405 (7)	5503 (28)
N16	4494 (6)	8963 (8)	6349 (34)
C17	4829 (6)	8812 (11)	7308 (35)
C18	4466 (7)	9612 (9)	5542 (36)
N19	3518 (5)	7691 (8)	3478 (31)
C20	3333 (6)	8205 (13)	2496 (37)
C21	3366 (7)	7012 (11)	3375 (36)



H atoms did not appear on a difference synthesis. On the 7 and 11 sites, we were unable to distinguish between oxygen or nitrogen and the structure was refined with a mean form factor for these two atoms. The table gives the atomic coordinates. A list of thermal parameters, bond distances and valency angles has been deposited with the Cambridge Crystallographic Data File.

SPECTRAL DATA (6, R'=H, R=CH_3)

NMR (δ, $CDCl_3$). S, s=singlet, D = doublet, Q, q=quadruplet, m=multiplet ^{1}H = 2' and 4' $N\langle^{CH_3}_{CH_3}$ (12H) two s at 2.82 and 2.94 ppm ; 1 and 3 N-CH_3 (6H) two s at 3.24 and 3.32 ppm ; -CH (1H) s at 5.02 ppm ; NH (1H) s at 7.65 ppm. ^{13}C : 1 and 3 N-CH_3, two Q at 28.8 and 30.5 ppm (^1J = 142 Hz); 2' and 4' $N\langle^{CH_3}_{CH_3}$, two Q of q at 38.2 and 40.8 ppm (^1J = 142 Hz); 5 C(spiro), S of m at 78.8 ppm ; 3'CH, D of s at 91.3 ppm (^1J = 170,6 Hz); 2 C=O, S of septuplet at 151.1 ppm ; 4 C=NH, S of m at 160.1 ppm ; 4 C=O, S of q at 166.9 ppm ; 2' and 4' C-N, S of m at 166.4 and 172.6 ppm ; M^+ = 292.

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(Received in UK 2 June 1980)