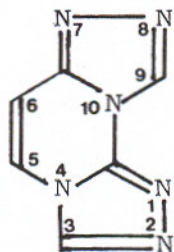
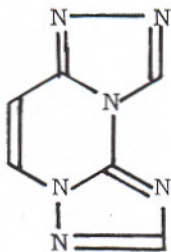


BIS-*s*-TRIAZOLO[4,3-*a*:4',3'-*c*]PYRIMIDINE AND RELATED SYSTEMSBy Desmond J. Brown and Tomohisa NagamatsuMedical Chemistry Group, John Curtin School of Medical Research,
P.O. Box 334, Canberra City, Australia 2601

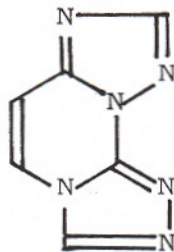
In extending our work on simple bicyclic *s*-triazolopyrimidines¹ to the tricyclic bis-*s*-triazolopyrimidines, e.g. (1), we encountered a meagre and confused literature. In retrospect, we know that all three such compounds described as derivatives of system (1) by La Noce and Giuliani² were, in fact, isomers in system (3) because a common intermediate³ had undergone an unexpected Dimroth-like rearrangement; that the 9-methyl and 9-trifluoromethyl derivatives of system (2), described by Reimlinger,⁴ were correctly formulated; and that Karp and Portnyagina⁵ had formulated their product correctly as the 5-methyl derivative of system (1) while naming it incorrectly as an isomer in the then-unknown system (4).



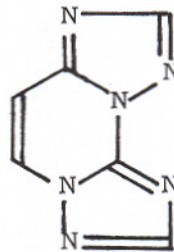
(1)



(2)



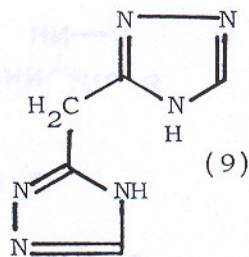
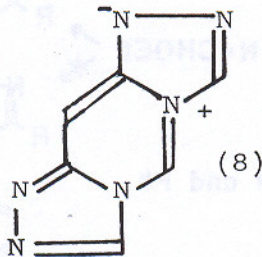
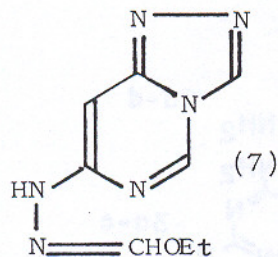
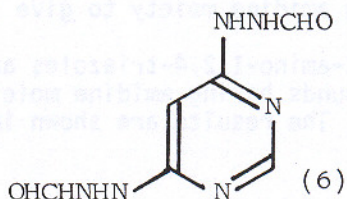
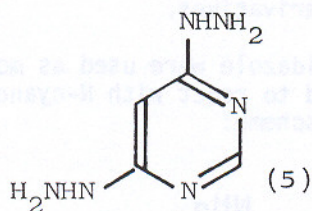
(3)



(4)

We now report synthetic routes to the parent compounds (1)-(3) and/or their simple *C*-methylated derivatives. Structures were confirmed by additional unambiguous syntheses and/or by n.m.r. spectral comparisons with

appropriate *s*-triazolo[4,3-*a*]pyrimidines and their [1,5-*a*], [4,3-*c*], and [1,5-*c*] isomers of unequivocal configuration. The systems (1)-(3) proved unexpectedly stable towards rearrangement in acid or alkali but the 3,9-dimethyl and 3,5,9-trimethyl derivatives of (1) did undergo thermal Dimroth rearrangement into the corresponding derivatives of (2). System (4) has eluded synthesis to date.



Attempts to prepare an abnormal (zwitterionic) bis-*s*-triazolopyrimidine, e.g. (8), from 4,6-dihydrazinopyrimidine (5) gave only the intermediates (6) and (7) or a product (9) from degradation of the postulated system.

1. Brown and Nagamatsu, *Aust. J. Chem.*, 1977, 30, 2515; 1978, 30, 2505.
2. La Noce and Giuliani, *J. Heterocycl. Chem.*, 1975, 12, 551.
3. Camerino, Palamidessi, and Sciaky, *Gazz. Chim. Ital.*, 1960, 90, 1821.
4. Reimlinger, *Chem. Ber.*, 1970, 103, 3278.
5. Karp and Portnyagina, *Khim.-Farm. Zh.*, 1970, 4, 29.