Dibenzo[1,2,3-*df*]triazepine

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Summary The first 1,2,3-triazepine, dibenzo[1,2,3-*df*]triazepine, has been isolated; its reactions account for the complexity of diazotisation of 2,2′-diaminobiphenyl.

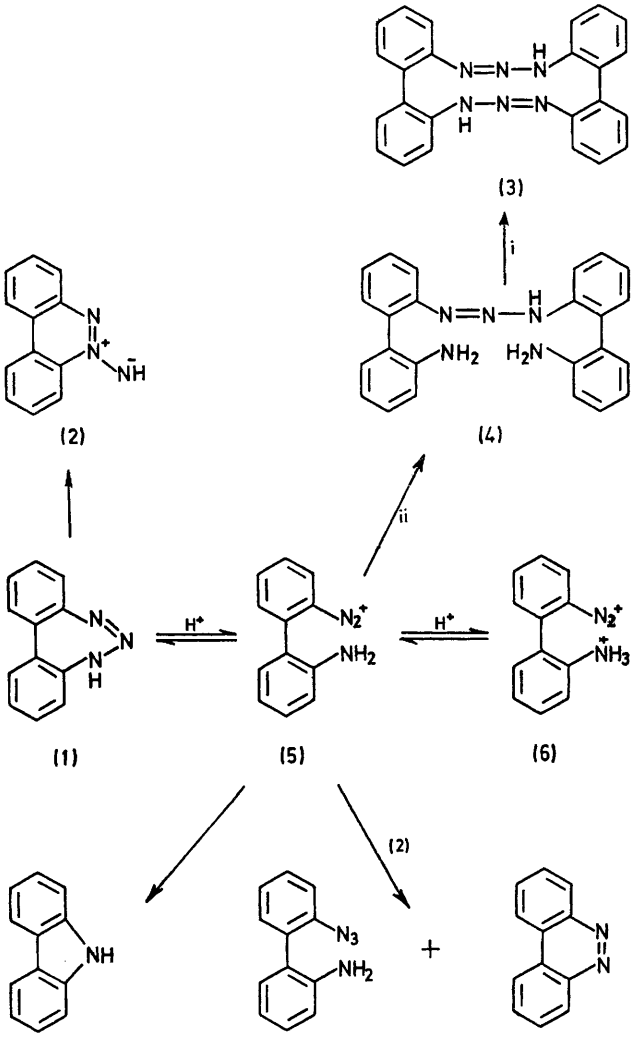
We have previously suggested that dibenzo[1,2,3-*df*]triazepine (**1**) is an intermediate in the formation of the *N*-iminobenzocinnolinium ylide (**2**) from 2,2′-diaminobiphenyl and pentyl nitrite in refluxing benzene.[1] We have now confirmed this by isolation of the triazepine (**1**) which is the first example of the 1,2,3-triazepine system.†

The triazepine‡ is obtained as a pale yellow solid (70%), m.p. 99—100°, by addition of an excess of dilute aqueous ammonia to a solution of tetrazotised 2,2′-diaminobiphenyl in 2N-HCl at 0°. Similar treatment of tetrazotised 1,8-diaminonaphthalene gave naphtho[1,8-*de*]triazine.

Triazepine (**1**) shows a sharp N–H i.r. stretching absorption (3270 cm^{-1}) and in this respect resembles linear diaryl triazenes rather than naphthotriazine. No diazonium cation absorption is observed. Its u.v. spectrum, λ_{max} 239, 265, and 294 nm (ϵ 27,300, 9750, and 5850), is consistent with a twisted biphenyl system. Chemical support for the proposed structure comes from a positive test with alkaline β-naphthol (masked diazonium compound), the formation of carbazole (95%) on thermal decomposition in refluxing diglyme, and rapid rearrangement of (**1**) to the ylide (**2**) in refluxing benzene.

The triazepine (**1**) is less stable than linear diaryl triazines and much less stable than naphtho[1,8-*de*]triazine possibly owing to a combination of angle strain and lack of aromatic stabilisation.

Its reactivity largely explains why diazotisation of 2,2′-diaminobiphenyl is complex and very dependent on experimental conditions. Thus pentyl nitrite in refluxing benzene gives ylide (**2**) whilst in refluxing methylene chloride containing catalytic quantities of HCl (as in some batches of commercial CH_2Cl_2) the bis-triazene (**3**) is obtained; this too represents a new heterocyclic ring system. Diazotisation with sodium nitrite in aqueous acetic acid gives carbazole, and diazotisation in 2N-HCl followed by basification with ammonia gives a mixture of ylide (**2**), linear triazene (**4**), 2-amino-2′-azidobiphenyl, benzocinnoline, and a trace of the bis-triazene (**3**), after chromatography on basic alumina. Triazepine (**1**) has been detected (t.l.c.) as a primary product in some of these reactions and suitable control experiments show that all products can be accounted for in terms of initial formation of (**1**) or its ring-opened conjugate acid (**5**). Surprisingly, although triazepine (**1**) rapidly gives carbazole in aqueous acetic acid, it is recovered unchanged from its solution in 2N hydrochloric or 50% sulphuric acid. Presumably in the stronger acid it is converted into the stable dication (**6**).



Reagents: i, pentyl nitrate; ii, 2,2′-diaminobiphenyl

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† A dihydrotriazepine structure has been suggested recently on the basis of rather limited evidence by L. A. Paquette and R. J. Haluska, *J. Amer. Chem. Soc.*, 1972, **94**, 534.

‡ Satisfactory analytical and mass spectral data were obtained for all new compounds reported.

[1] S. F. Gait, C. W. Rees, and R. C. Storr, *Chem. Comm.*, 1971, **1545**.