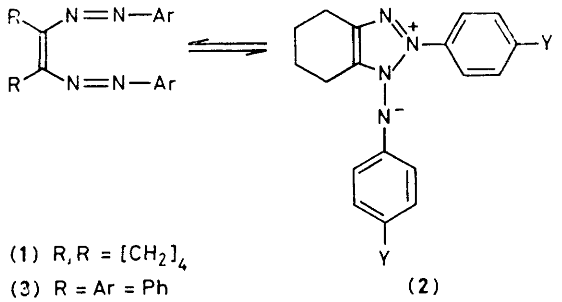
A New Fused Tricyclic Tetra-aza[4.3.3.0^{1,6}]dodecene System: Substituted 3,3a,4,5,6,6a-Hexahydropyrrolo[2,3-*d*]-1,2,3-triazoles from the Reaction of Acrylonitrile with *cis*-1,2-Bis(areneazo)ethylenes and a Re-assessment of 1,3-Cycloaddition Products

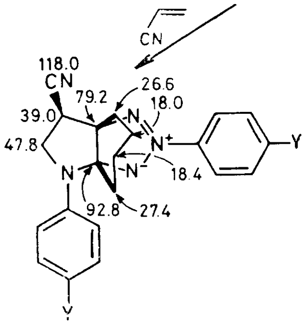
Richard N. Butler,* D. Cunningham, John P. James, and Patrick McArdle
Chemistry Department, University College, Galway, Ireland

The thermal reaction of *cis*-1,2-bis(areneazo)ethylenes with acrylonitrile gave substituted 3,3a,4,5,6,6a-hexahydropyrrolo[2,3-*d*]-1,2,3-triazoles with a saturated bridgehead which, when fused to a cyclohexyl ring, constituted a tricyclic tetra-azadodecene structure; these products could not arise directly from 1,3-dipolar cycloadditions.

cis-Bis(areneazo)ethylenes exist as isomeric mixtures of structures (**1**) and (**2**),[1-3] both of which we have recently directly detected[4] in dynamic equilibrium. The presence of form (**2**) had been correctly inferred[3] from trapping in a range of 1,3-dipolar cycloadditions with dienophiles A=X giving adducts which were assigned the general structure (**10**). Reactions of *cis*-bis(areneazo)ethylenes often give rise to unexpected products.[5-7] Cyclohexene derivatives (**1**) have not been examined previously and we now find that the addition reactions of these with acrylonitrile gave a new ring system, the unexpected products (**4**).

When compounds (**1a**) and (**1b**) were treated with acrylonitrile in acetone† the adducts obtained in high yield showed two quaternary C–N carbon signals and no –C≡N signal in their ^{13}C n.m.r. spectra (Scheme 1). A structure such as (**10**) could not accommodate these shifts. Normal ^{1}H n.m.r. and other spectra were of limited value for the structural determination of these compounds owing to the variety of possible closely related adducts of the (**1**) ⇌ (**2**) system. A full *X*-ray crystallographic analysis‡ of the product from acrylonitrile and compound (**1a**) showed that a multi-step reaction had occurred involving N–N bond cleavage and N–C bond formation. The product had the novel tricyclic structure (**4a**) with a saturated C–C bridgehead thus making it a derivative of 7,8,9,10-tetra-azatricyclo[4.3.3.0^{1,6}]dodec-7-ene (Figure 1). The product from the same reaction with (**1b**) was (**4b**). The basic structural unit of the compounds (**4**) is a new reduced aziminoazapentalene[8] system, a substituted 3,3a,4,5,6,6a-hexahydropyrrol[2,3-*d*]-1,2,3-triazole. Since these products did not have the expected structure of type (**10**) we re-examined some of the cycloaddition reactions of a normal acyclic *cis*-bis(areneazo)alkene. Thus the reaction of *cis*-1,2-diphenyl-1,2-bis(benzeneazo)ethylene, (**3**), with acrylonitrile under a variety of conditions gave the product (**6**) which has previously[3] been assigned structure (**5**) from a 1,3-dipolar cycloaddition. The comparable reaction of compound (**3**) with ethyl acrylate, dimethyl acetylenedicarboxylate, and maleic anhydride gave the compounds (**7**), (**8**), and (**9**), respectively. Compounds (**6**)—(**9**) are analogous to the structures (**4**). They showed all





(**4**)
a; Y = H
b; Y = NO$_2$

Scheme 1. ^{13}C N.m.r. shifts from Me$_4$Si in CDCl$_3$ shown for (**4a**).

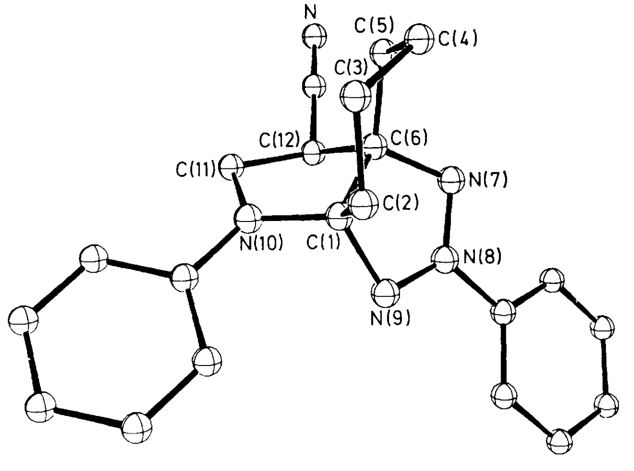
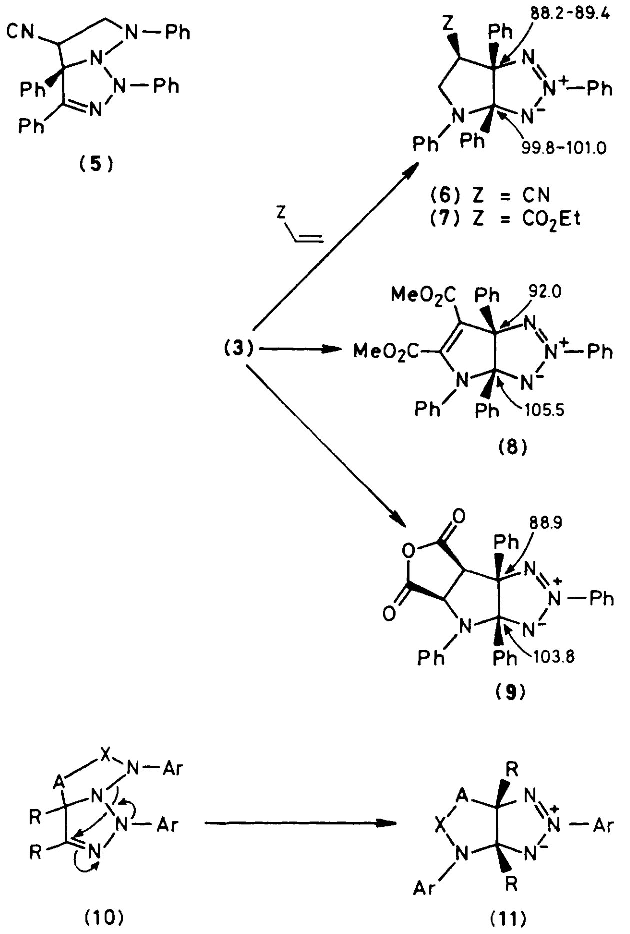


Figure 1. *X*-Ray structure of compound (**4a**) (hydrogen atoms omitted).

---

† A solution of the 1,2-bis(areneazo)ethylene (300 mg) in acetone (10 ml) or chloroform was treated with acrylonitrile (≥1 mol), heated under reflux for 30 min, and evaporated under reduced pressure. Crystallisation of the residue from ethanol gave the products (**4a**), m.p. 168 °C (88%); (**4b**), m.p. 214 °C (80%) (**6**), m.p. 269 °C (90%) (**7**), m.p. 210 °C (87%) (**8**), m.p. 187 °C (85%); (**9**), m.p. 224 °C (80%).

‡ *Crystal data* for (**4a**): $C_{21}H_{20}N_5$, triclinic, a = 9.328 (2), b = 10.925 (3), c = 11.462 (3) Å, α = 64.84 (4), β = 86.57 (4), γ = 115.37 (4)°, space group $P\bar{1}$, Z = 2, R = 0.0408, R_w = 0.0662 for 1511 independent reflexions having $I > 5\sigma(I)$, number of parameters = 238. The *X*-ray structure is shown in Figure 1. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



Scheme 2. ^{13}C N.m.r. shifts from Me_4Si in $CDCl_3$ shown.

of the expected ^{13}C n.m.r. signals including the key quaternary bridgehead carbons (Scheme 2). They have all previously been assigned structures of type (**10**).

A large number of other compounds have been assigned the general structure (**10**) in the literature from the reactions of dienophiles, A=X, with *cis*-bis(areneazo)alkenes.[7] In the light of the results herein the structures of many or all of these need to be re-assessed and they will probably prove to have the general structure (**11**) as did the products (**4**), (**6**), (**7**), (**8**), and (**9**). While compounds of the general type (**11**) could not arise directly from 1,3-dipolar cycloadditions they could still arise indirectly from such cycloadditions *via* compounds of type (**10**), for example (**5**), as shortlived intermediates. However, attempts to intercept compound (**5**) by carrying out the reaction of compound (**3**) with acrylonitrile at ambient temperatures, 0 °C and 20 °C, were not successful. As the temperature was progressively lowered either no reaction occurred during the prolonged stirring or compound (**6**) only was isolated in lower yields.

J. P. J. acknowledges an Irish Government Grant for Research.

Received, 31st March 1983; Com. 426

References

1 G. S. Angadiyavar, K. B. Sukumaran, and M. V. George, *Tetrahedron Lett.*, 1971, 633.

2 K. B. Sukumaran, S. Satish, and M. V. George, *Tetrahedron*, 1974, **30**, 445.

3 K. B. Sukumaran, C. S. Angadiyavar, and M. V. George, *Tetrahedron*, 1972, **28**, 3987.

4 R. N. Butler and J. P. James, *J. Chem. Soc., Chem. Commun.*, 1983, 627.

5 H. Bauer, A. J. Boulton, W. Fedeli, A. R. Katritzky, A. Majid-Hamid, F. Mazza, and A. Vaciago, *J. Chem. Soc., Perkin Trans.* 2, 1972, 662.

6 N. E. Alexandrou and E. D. Micromastoras, *Tetrahedron Lett.*, 1968, 231.

7 M. V. George, A. Mitra, and K. B. Sukumaran, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 973.

8 For a review of azapentalene systems see, J. Elguero, R. M. Claramount, and A. J. H. Summers, *Adv. Heterocycl. Chem.*, 1978, **22**, 183.