2,3,5,6-Tetra-aryl-1,2,4,5-tetra-azapentalenes.[1] A New Heteroaromatic System

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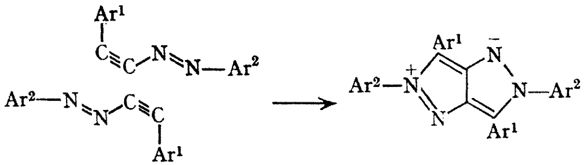
Summary Arylazoethynylarenes, on heating in solution, dimerize to give 2,3,5,6-tetra-aryl-1,2,4,5-tetra-azapentalenes (II), a very stable new heteroaromatic system.

p-CHLOROPHENYLAZOETHYNYLBENZENE, (I; Ar^1 = Ph, Ar^2 = *p*-$Cl{\cdot}C_6H_4$), prepared from *p*-chlorobenzenediazonium chloride and silver phenylacetylide,[2] on prolonged heating in boiling cyclohexane deposited pale yellow crystals (60%), $C_{28}H_{18}Cl_2N_4$, m.p. 328°, λ_{max} (benzene) 297 and 408 nm (log ϵ 4·17 and 4·05), and mass-spectral *M*, 480.

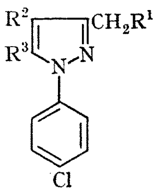
It is sparingly soluble in ordinary organic solvents giving strongly fluorescent solutions, but dissolves readily in concentrated sulphuric acid and is re-precipitated by diluting with water. It is unaffected by heating under reflux in 65% sulphuric acid and can be sublimed *in vacuo* at about 300°. With silver nitrate in a mixture of acetonitrile and tetrahydrofuran it gives a 1 : 1 adduct, $C_{28}H_{18}Cl_2N_4,AgNO_3$, m.p. 314° (decomp.).

The structure of this compound has been shown to be 3,6-diphenyl-2,5-bis-(*p*-chlorophenyl)-1,2,4,5-tetra-azapentalene, (II; Ar^1 = Ph, Ar^2 = *p*-$Cl{\cdot}C_6H_4$), from its mode of formation and the following degradations.

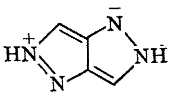
Its pyrolysis *in vacuo* at about 500° afforded pale yellow needles (30%), m.p. 93°, identified with α-(*p*-chlorophenylimino)phenylacetonitrile by mixed m.p. with an authentic specimen[3] and by comparison of the i.r. spectra. Catalytic hydrogenation of (II) with platinum oxide in acetic acid at 60° gave two pyrazole derivatives, $C_{24}H_{26}ClN_3O$ (III, 25%), m.p. 233—235° (dec.), and $C_{24}H_{32}ClN_3O$ (IV, 10%), m.p. 214—215°. Compound (III) was assigned the structure 4-acetamino-1-*p*-chlorophenyl-3-cyclohexylmethyl-5-phenylpyrazole on the basis of spectral and analytical data and of degradation, and (IV), consequently, is 4-acetamino-1-*p*-chlorophenyl-5-cyclohexyl-3-cyclohexylmethylpyrazole. Hydrolysis of



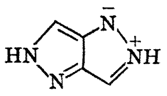
(I) (II)



	R^1	R^2	R^3
(III)	C_6H_{11}	AcNH	Ph
(IV)	C_6H_{11}	AcNH	C_6H_{11}
(V)	C_6H_{11}	H	Ph
(VI)	Ph	H	Ph



(VII)



(VIII)

(III) and deamination of the resulting amine by reduction of the corresponding diazonium tetrafluoroborate with sodium borohydride yielded needles, $C_{22}H_{23}ClN_2$, m.p. 113—114°, identified as 1-*p*-chlorophenyl-3-cyclohexylmethyl-5-phenylpyrazole (V) on the basis of a separate synthesis of this compound by condensation of *p*-chlorophenylhydrazine with 1,4-diphenylbutane-1,3-dione to give 3-benzyl-1-*p*-chlorophenyl-5-phenylpyrazole (VI), m.p. 111—112°, followed by catalytic hydrogenation. Evidence for the presence of a cyclohexylmethyl instead of a benzyl group in (V) is furnished by its n.m.r. spectrum (60 MHz.) in deuteriochloroform with a doublet signal at δ 2·59 (2H, *J* 6 Hz.), whereas the n.m.r. spectrum of (VI) shows a singlet at δ 4·06 due to a benzylic methylene.

The tetra-azapentalenes listed in the Table have been prepared by similar dimerization. Satisfactory elemental analyses and supporting spectral data have been obtained for all compounds reported.

The parent structure, 2*H*,5*H*-pyrazolo[4,3-*c*]pyrazole, is meso-ionic, being satisfactorily represented only by several charge-separated structures such as (VII) and (VIII).

TABLE: *Tetra-azapentalenes* (II)

Ar^1	Ar^2	M.p.
Ph	*p*-Br·C_6H_4	342—343°
Ph	*p*-NO_2·C_6H_4	358—359°
p-NO_2·C_6H_4	*p*-Cl·C_6H_4	>340°
p-Br·C_6H_4	*p*-Cl·C_6H_4	349°
p-Br·C_6H_4	*p*-NO_2·C_6H_4	>370°
p-Me·C_6H_4	*p*-Cl·C_6H_4	321°
p-Me·C_6H_4	*p*-NO_2·C_6H_4	354—355°

Evidently, the nucleus contains a total of ten π-electrons distributed over the two rings; accordingly an aromatic character similar to azulene or naphthalene is expected.

(*Received, September 26th*, 1969; *Com.* 1456.)

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[1] The parent structure may be named 2*H*,5*H*-pyrazolo[4,3-*c*]pyrazole. Substituted 1*H*,4*H*-pyrazolo[4,3-*c*]pyrazoles have been prepared by D. G. Farnum and P. Yates, *J. Amer. Chem. Soc.*, 1962, **84**, 1399.

[2] A. M. Sladkov, L. Yu. Ukhin, and G. N. Gorshkova, *Zhur. org. Khim.*, 1966, **2**, 1456 [*Chem. Abs.*, 1967, **66**, 55143s].

[3] O. Mumm, *Ber.*, 1910, **43**, 886.