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

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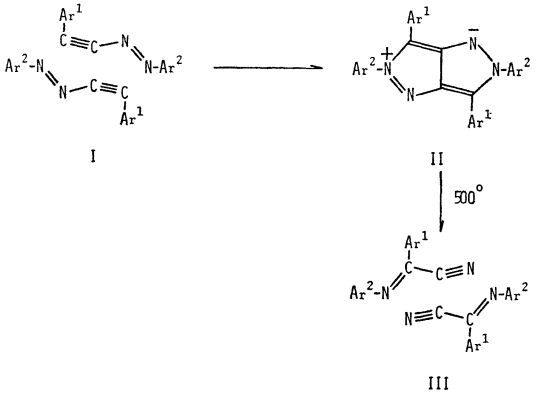
2,3,5,6-Tetra-aryl-1,2,4,5-tetra-azapentalenes (II) have been prepared by the dimerization of arylazoethynylarenes (I). The properties of the new ring system are discussed on the basis of their reactivities.

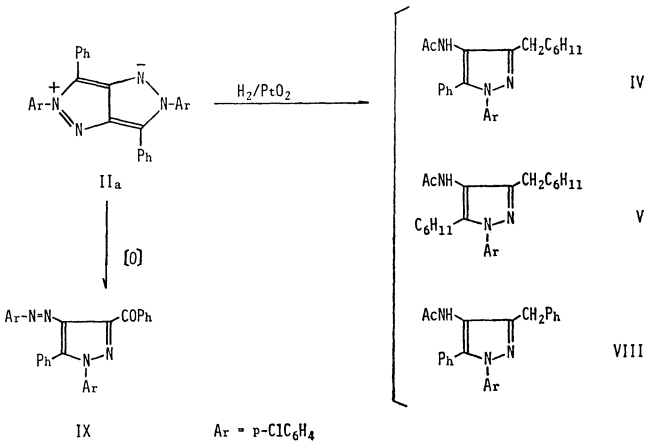
1-Methylpentalene[2] was found so unstable as to dimerize even at −100 °C, but pentalene dianion,[3] a 10π-electron system, is known to show aromatic character. Thus, replacement of the ring carbon atoms of pentalenes by nitrogen atoms may yield stable azapentalenes containing 10π-electrons. We have recently synthesized 2,3,5,6-tetra-aryl-1,2,4,5-tetra-azapentalenes[4] (II) and 2-aryl-5-phenyl-*v*-triazolo[4,5-*d*]-*v*-triazoles,[5] both new *meso*-ionic heteroaromatics. These azapentalenes contain nitrogens at non-fused positions and examples of *meso*-ionic azapentalenes with nitrogens at fused positions have recently been described.[6] This paper presents the synthesis, structure, and properties of 2,3,5,6-tetra-aryl-1,2,4,5-tetra-azapentalenes.

p-Chlorophenylazoethynylbenzene[7] (Ia: Ar^1=Ph, Ar^2=*p*-ClC_6H_4), prepared from *p*-chlorobenzenediazonium chloride and silver phenylacetylide, on heating in cyclohexane deposited 2,5-bis-(*p*-chlorophenyl)-3,6-diphenyl-1,2,4,5-tetra-azapentalene (IIa: Ar^1=Ph, Ar^2=*p*-ClC_6H_4) in 60% yield. This compound shows ultraviolet absorption maxima at 292 and 398 nm (log ε=4.37 and 4.33, respectively) in chloroform. Tetra-azapentalene IIa is pale yellow crystalline solid, mp 328 °C, which is sparingly soluble in ordinary organic solvents giving strongly fluorescent solutions. It is weakly basic, being insoluble in dilute mineral acids, but dissolves readily in concentrated sulphuric acid and is reprecipitated when the solution is diluted with water. It is unaffected by heating in 65% sulphuric acid and can be sublimed unchanged *in vacuo* at about 300 °C. On prolonged heating with methyl iodide, it gives a crystalline methiodide, which is decomposed into its components at about 200 °C or when dissolved in solvents other than methyl iodide. Treatment of tetra-azapentalene IIa with silver nitrate in a mixture of acetonitrile and tetrahydrofuran gives a 1 : 1 adduct, mp 314 °C (decomp.).

Evidence for the structure of compound IIa was provided by its mode of formation, its spectral and analytical data, and the following degradations.

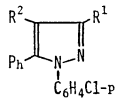


Its pyrolysis *in vacuo* at about 500 °C afforded pale yellow needles (26%), mp 93.5—94.5 °C, identified with α-(*p*-chlorophenylimino)phenylacetonitrile[8] (IIIa: Ar^1=Ph, Ar^2=*p*-ClC_6H_4).



When compound IIa was hydrogenated in acetic acid at 60 °C with platinum oxide, two pyrazole derivatives, $C_{24}H_{26}ClN_3O$ (IV, 25%), mp 233—235 °C (decomp.), and $C_{24}H_{32}ClN_3O$ (V, 10%), mp 214—215 °C, were isolated, and they were assigned the structures of 4-acetamino-1-*p*-chlorophenyl-3-cyclohexylmethyl-5-phenylpyrazole (IV) and 4-acetamino-1-*p*-chlorophenyl-5-cyclohexyl-3-cyclohexylmethylpyrazole (V), respectively, on the basis of their spectral and analytical data and of the degradation of compound IV. Hydrolysis of compound IV and deamination of the resulting amine by reduction of the corresponding diazonium fluoroborate with sodium borohydride yielded 1-*p*-chlorophenyl-3-cyclohexylmethyl-5-phenylpyrazole (VI), mp 113—114 °C. The structure of this compound was established by an independent synthesis, in which condensation of *p*-chlorophenylhydrazine with 1,4-diphenylbutane-1,3-dione in ethanol yielded 3-benzyl-1-*p*-chlorophenyl-5-phenylpyrazole (VII), mp 111—112 °C. Catalytic hydrogenation of this pyrazole (VII) with platinum oxide in acetic acid at room temperature gave a product, which was identical with compound VI. Evidence for the presence of a cyclohexylmethyl instead of a benzyl group in compound VI is furnished by its NMR spectrum with a doublet at τ 7.41 (2H, J=6 Hz), whereas the NMR spectrum of compound VII shows a singlet at τ 5.94 due to a benzylic methylene. The observed spectral data are not incompatible with the isomeric structure of 1-*p*-chlorophenyl-5-cyclohexylmethyl-3-phenylpyrazole, which could be expected from

the above synthetic route. However, the fact that compound VI was obtained from the degradation of IIa excludes such an assignment to VI, and thus, supports the structure of 3-benzyl-1-*p*-chlorophenyl-5-phenylpyrazole for compound VII. Separate hydrogenation of IIa under similar conditions resulted in the cleavage of the parent ring to give another pyrazole derivative, 4-acetamino-3-benzyl-1-*p*-chlorophenyl-5-phenylpyrazole (VIII, 12%), mp 217—218 °C. Comparison of the NMR spectra of VII and VIII (a singlet signal at τ 5.90 due to a benzylic methylene) reveals their close similarity, and supports the above structure for compound VIII.



VI: $R^1 = C_6H_{11}CH_2$, $R^2 = H$
VII: $R^1 = PhCH_2$, $R^2 = H$
XI: $R^1 = PhCO$, $R^2 = NH_2$

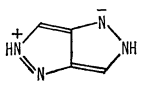
Compound IIa was oxidized with potassium permanganate in a mixture of pyridine and water at 95 °C to yield 3-benzoyl-1-*p*-chlorophenyl-4-*p*-chlorophenylazo-5-phenylpyrazole (IX, 64%), mp 208—209.5 °C, the structure being determined on the basis of its spectral and analytical data and of its degradation. The IR spectrum of IX shows a band at 1665 cm^{-1} due to a carbonyl stretching vibration. The NMR spectrum shows a multiplet at τ 2.4—2.7. The mass spectrum shows the molecular ion *m/e* 496, and major fragments *m/e* 385($M^+ - C_6H_4Cl$), 105(C_6H_5CO), and 77(C_6H_5). Compound IX was hydrogenated in acetic acid with 10% palladium on carbon to yield two products, 4-acetamino-3-benzyl-1-*p*-chlorophenyl-5-phenylpyrazole (VIII, 12%) and 4-amino-3-benzoyl-1-*p*-chlorophenyl-5-phenylpyrazole (XI, 16%), mp 182 °C. With peroxyacetic acid in chloroform, compound IIa also gave this arylazobenzoylpyrazole (IX, 9%).

Nitration of compound IIa with nitric acid (*d*= 1.38) in concentrated sulphuric acid at room temperature gave a dinitro derivative (IId: Ar^1=*p*-NO_2-C_6H_4, Ar^2=*p*-ClC_6H_4), mp 365 °C.

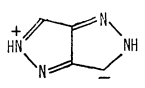
Treatment of compound IIa with bromine in chloroform gave a monobromo derivative (XII, 38%), mp 294.5—295.5 °C, together with a small quantity (6%) of a dibromo derivative (IIe: Ar^1=*p*-BrC_6H_4, Ar^2=*p*-ClC_6H_4), mp 349 °C. The structures of IId and IIe were substantiated by separate syntheses through dimerization of 4-(*p*-chlorophenylazoethynyl)-substituted nitro- and bromobenzene, respectively. The monobromide (XII) was assigned the structure of 2,5-bis-(*p*-chlorophenyl)-3-*p*-bromophenyl-6-phenyl-1,2,4,5-tetra-azapentalene. The position of the bromo substituent in the benzene ring was established by examination of the IR spectrum (ν_{max} 760 and 675 cm^{-1}, and 840 cm^{-1} due to mono- and 1,4-disubstituted benzene, respectively).

The tetra-azapentalenes listed in the Table have been prepared by dimerization of arylazoethynylarenes.

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 XIII and XIV. The preferential electrophilic substitution observed at the *para* positions in the phenyl substituents of compound IIa indicates an electron-donating character of the parent structure due to the contribution of resonance structures such as XIV.



XIII



XIV

Experimental

*2,5-Bis-(*p*-chlorophenyl)-3,6-diphenyl-1,2,4,5-tetra-azapentalene (IIa).* A solution of *p*-chlorophenylazoethynylbenzene (Ia, 6.0 g) in 200 ml of cyclohexane was heated under reflux for 5 hr, and the solvent was removed by distillation. The crystalline residue was washed with acetone and recrystallized from benzene to yield 3.6 g (60%) of compound IIa (Found: C, 69.88; H, 3.77; N, 11.92%. Calcd for $C_{28}H_{18}Cl_2N_4$: C, 69.86; H, 3.77; N, 11.64%), mp 328 °C; λ_{max} (chloroform) 292 and 398 (log ε 4.37 and 4.33, respectively), and mass-spectral M, 480.

Other tetra-aryl-tetra-azapentalenes prepared in similar ways are listed in Table 1.

*2,5-Bis-(*p*-chlorophenyl)-3,6-diphenyl-1-methyl-1,2,4,5-tetra-azapentalenium Iodide.* A mixture of IIa (0.90 g) and methyl iodide (50 ml) was heated under reflux for one week. The mixture was filtered and the filtrate, on evaporation of solvent, gave 0.90 g (77%) of the methiodide as orange crystals. The crude material was dissolved in methyl iodide and the solvent was removed under reduced pressure. The residual crystals were similarly treated repeatedly with methyl iodide, and subjected to analysis (Found: C, 56.05; H, 3.51; N, 8.71%. Calcd for $C_{28}H_{18}Cl_2N_4 \cdot CH_3I$: C, 55.88; H, 3.40; N, 8.99%) The methiodide, heated at about 200 °C or dissolved in solvents other than methyl iodide, decomposed into methyl iodide and compound IIa.

Complex Formation of Compound IIa with Silver Nitrate. To a solution of compound IIa (0.22 g) in 100 ml of tetrahydrofuran was added a solution of silver nitrate (1.0 g) in 20 ml of acetonitrile. The mixture was stirred for 3 hr at room temperature, and the pale yellow precipitate was collected and washed with fresh acetonitrile and tetrahydrofuran to yield 0.3 g of the silver nitrate complex. Recrystallization from dimethylformamide gave a pure sample (Found: C, 52.00; H, 2.62; N, 11.02%. Calcd for $C_{28}H_{18}Cl_2N_4 \cdot AgNO_3$: C, 51.64; H, 2.79; N, 10.75%), mp 314 °C (decomp.).

Pyrolysis of Compounds IIa and IIb. α-(p-Chlorophenylimino)- and α-(p-Bromophenylimino)phenylacetonitrile (IIIa and IIIb): Compound IIa (1.2 g), when heated at about 500 °C under reduced pressure of 1 mmHg in a quartz tube, deposited yellow silky crystals on a cold part of the tube. The organic materials were dissolved in ether, and subjected to chromatography on silica gel in benzene. Evaporation of the eluate followed by recrystallization from ethanol gave 0.31 g (26%) of compound IIIa as yellow needles (Found: C, 70.37; H, 4.24; N, 11.66%. Calcd for $C_{14}H_9ClN_2$: C, 69.86; H, 3.77; N, 11.64%), mp 93.5—94.5 °C (lit,[8] mp 94 °C), ν_{max} (KBr) 1595, 1570, 1480, 1445, 1280, 1090, 1015, 1000, 835, 770, 740, 680, and 520 cm^{-1}. The product was identical (mixed melting point, and IR spectrum) with an authentic specimen.

Pyrolysis of compound IIb (1.0 g) in a similar way gave 0.159 g of α-(*p*-bromophenylimino)phenylacetonitrile[9] (Found: C, 59.16; H, 2.88; N, 10.00%. Calcd for $C_{14}H_9BrN_2$: C, 58.97; H, 3.18; N, 9.83%), mp 115.0—115.5 °C (lit,[9] mp 118 °C); ν_{max} (KBr) 1595, 1570, 1475, 1445, 1280, 1200, 1065, 1010, 840, 775, 740, 685, and 520 cm^{-1}.

TABLE 1. TETRA-AZAPENTALENES (II)

II	X in Ar^1 (p-XC_6H_4)	X in Ar^2 (p-XC_6H_4)	Mp (°C)	Yield (%)	Formula		Elementary analysis (%) C	H	N	λ_{max} ($CHCl_3$) nm (log ε)
IIa	H	Cl	328	60	$C_{28}H_{18}Cl_2N_4$	Found	69.86	3.77	11.64	292(4.37), 398(4.33)
						Calcd	69.88	3.77	11.92	
IIb	H	Br	342—343	50	$C_{28}H_{18}Br_2N_4$	Found	58.90	3.48	10.09	295(4.45), 398(4.33)
						Calcd	58.97	3.18	9.83	
IIc	H	NO_2	358—359	55	$C_{28}H_{18}N_6O_4$	Found	67.04	3.87	16.61	332(4.52), 439(3.96)
						Calcd	66.92	3.61	16.73	
IId	NO_2	Cl	>365	1	$C_{28}H_{16}Cl_2N_6O_4$	Found	59.34	2.92	13.95	270(3.43), 310(4.24),
						Calcd	58.86	2.82	14.71	448(4.53)
IIe	Br	Cl	349	40	$C_{28}H_{16}Br_2Cl_2N_4$	Found	52.64	2.47	8.63	292(4.31), 404(4.40)
						Calcd	52.61	2.52	8.77	
IIf	Br	NO_2	>370	40	$C_{28}H_{16}Br_2N_6O_4$	Found	50.78	2.61	12.68	330(4.54), 440(4.11)
						Calcd	50.93	2.44	12.73	
IIg	CH_3	Cl	321	50	$C_{30}H_{22}Cl_2N_4$	Found	71.02	4.60	10.70	292(4.40), 401(4.35)
						Calcd	71.26	4.35	11.00	
IIh	CH_3	NO_2	354—355	20	$C_{30}H_{22}N_6O_4$	Found	67.90	4.05	15.97	336(4.58), 448(3.98)
						Calcd	67.91	4.18	15.84	

Catalytic Hydrogenation of Compound IIa. (a) 4-Acetamino-1-p-chlorophenyl-3-cyclohexylmethyl-5-phenylpyrazole (IV) and 4-Acetamino-1-p-chlorophenyl-5-cyclohexyl-3-cyclohexylmethylpyrazole (V): A suspension of IIa (4.4 g) in 285 ml of acetic acid was hydrogenated over platinum oxide (0.44 g) with hydrogen (60 kg/cm²) at 60 °C for 2 days. The insoluble material was removed by filtration and the filtrate was concentrated under reduced pressure. The residue was poured into 100 ml of water and the mixture was neutralized with sodium bicarbonate. The brownish white solid was collected on a filter, washed with water, and dried. The crude product was chromatographed on silica gel in chloroform as eluant. Evaporation of the eluate followed by fractional recrystallization from ethanol gave two pyrazole derivatives: Compound VI (25 %) (Found: C, 70.89; H, 5.87; N, 10.38%. Calcd for $C_{24}H_{26}ClN_3O$: C, 70.66; H, 6.42; N, 10.30%), mp 233—235 °C (white needles), mass *m/e* 407 (M^+, 23%), 401(29), 359(17), 325(100), 283(17), 214(69), 141(15), 123(16), 111 (50), and 77(20); and compound V (10%) (Found: C, 69.81; H, 7.86; N, 10.02%. Calcd for $C_{24}H_{32}ClN_3O$: C, 69.63; H, 7.79; N, 10.15%), mp 214—215 °C (white leaflets), mass *m/e* 413 (M^+, 15%), 407(10), 331(100), 138(23), and 111(12).

(b) 4-Acetamino-3-benzyl-1-p-chlorophenyl-5-phenylpyrazole (VIII): Separate hydrogenation of IIa (1.0 g) over 0.1 g of platinum oxide with hydrogen (90 kg/cm²) at 60 °C for 47 hr followed by similar treatment to that described above yielded 0.1 g (12%) of compound VIII (Found: C, 71.71; H, 4.96; N, 10.31%. Calcd for $C_{24}H_{20}ClN_3O$: C, 71.73; H, 5.02; N, 10.46%), mp 217—218 °C (from chloroform and pentane).

Deamination of Compound IV. 1-p-Chlorophenyl-3-cyclohexylmethyl-5-phenylpyrazole (VI): Crude compound IV (1.0 g) was hydrolyzed by heating under reflux in 200 ml of 30% sulphuric acid for 45 min. After cooling, the solution was neutralized with aqueous sodium hydroxide, and the organic material was extracted with ether. After evaporation of the solvent, the residue was dissolved in a mixture of 8 ml of concentrated hydrochloric acid and 50 ml of water and treated with sodium nitrite (0.18 g) at 0—3 °C. The solution was stirred for 3 hr and filtered to remove insoluble matter. Fluoroboric acid (48%, 5 ml) was added to the filtrate, and the white precipitate of the resulting diazonium tetrafluoroborate was collected on a filter and washed with a small portion of tetrafluoroboric acid. Sodium borohydride (1 g) was added in small portions with stirring to a solution of the diazonium tetrafluoroborate in about 10 ml of dimethylformamide at 0—3 °C. Stirring was continued for 2 hr at 0 °C and for another 2 hr at room temperature. The reaction mixture was poured into a solution of 10 ml of concentrated hydrochloric acid and 20 ml of ice water. Gummy materials, which were separated by filtration were digested with ether, and the ethereal extract was evaporated to yield yellowish orange oil. The oil was chromatographed on silica gel in benzene. The eluate was concentrated and subjected to purification by preparative thin layer chromatography on silica gel. After development with benzene, the faster moving substance was collected and recrystallized from aqueous ethanol giving 4 mg of compound VI as white needles, mp 113.1—114.1 °C, which is identical (mixed mp and IR spectrum) with material described later.

3-Benzyl-1-p-chlorophenyl-5-phenylpyrazole (VII). A mixture of 1,4-diphenylbutane-1,3-dione (6.7 g) and *p*-chlorophenylhydrazine (5.4 g) in 75 ml of ethanol was heated under reflux for 3 hr. The reaction mixture was concentrated, and the product was separated by filtration and washed with dilute acetic acid and then with water. Recrystallization of the crude product from aqueous ethanol with active charcoal gave 7.4 g (77%) of compound VII (Found: C, 76.48; H, 4.90; N, 8.12%. Calcd for $C_{22}H_{17}ClN_2$: C, 76.62; H, 4.97; N, 8.13%), mp 109.2—110.2 °C (white needles).

Catalytic Hydrogenation of Compound VII. 1-p-Chlorophenyl-3-cyclohexylmethyl-5-phenylpyrazole (VI): A solution of compound VII (3.44 g) in 200 ml of acetic acid was hydrogenated with 0.4 g of platinum oxide with hydrogen (60 kg/cm²) for 48 hr. Removal of the catalyst and solvent left an oily residue. Chromatography on activated alumina in benzene gave a colourless oily product. Distillation at about 205 °C/1.5 mmHg gave 0.57 g (16.3%) of compound VI (Found: C, 75.53; H, 6.65; N, 7.68%. Calcd for

$C_{22}H_{23}ClN_2$: C, 75.31; H, 6.61; N, 7.99%, mp 113.1—114.5 °C; ν_{max} (KBr) 3050, 2920, 2840, 1595, 1550, 1490, 1440, 1370, 1170, 1095, 1000, 970, 830, 760, 700, 600, 560, 535, and 500 cm^{-1}.

*Oxidation of Compound IIa. 3-Benzoyl-1-*p*-chlorophenyl-4-*p*-chlorophenylazo-5-phenylpyrazole (IX). (a) With Potassium Permanganate*: To a mixture of compound IIa (2.50 g), 300 ml of pyridine, and 150 ml of water was added potassium permanganate (*ca.* 3 g) in small portions over a period of 4 days, the temperature being kept at about 95 °C. The resulting mixture was filtered while hot, and the filtrate was cooled to yield 1.60 g (64%) of 3-benzoyl-1-*p*-chlorophenyl-4-chlorophenylazo-5-phenylpyrazole (IX) (Found: C, 67.49; H, 3.80; N, 10.98%. Calcd for $C_{28}H_{18}Cl_2N_4O$: C, 67.62; H, 3.65; N, 11.26%), mp 208—209.5 °C (yellow needles from ethanol and acetone); λ_{max} (ethanol) 244 and 344 nm (log ε=4.65 and 4.33, respectively); mass *m/e* 496(M^+, 38%), 385(64), 214(53), 141(44), 105(82), and 77(100).

(b) With Peroxyacetic Acid: Compound IIa (1.50 g) in a mixture of 200 ml of chloroform and 280 ml of a solution (total activity, 2.2%) prepared from 30 ml of 30% hydrogen peroxide and 300 ml of acetic acid was heated under reflux for 11 hr. The mixture was cooled and poured into a large amount of cold aqueous sodium hydroxide solution. The organic layer was separated and evaporated to dryness. The residue was treated as described above to yield 0.13 g (9%) of compound IX and some starting material.

*Catalytic Hydrogenation of Compound IX. 4-Amino-3-benzoyl-1-*p*-chlorophenyl-5-phenylpyrazole (XI)*: Compound IX (0.82 g) in 100 ml of acetic acid was hydrogenated over 0.10 g of 10% palladium on carbon at a hydrogen pressure of 70 kg/cm^2 at 45 °C for 17 hr. The insoluble material was removed by filtration, and the filtrate was concentrated to dryness under reduced pressure. The residue was digested with ether and the ethereal extract was washed with dilute aqueous sodium bicarbonate. The ether was evaporated, and the residue was chromatographed on silica gel in dichloromethane and eluted with ether. The faster moving fraction gave 100 mg (16%) of compound XI on recrystallization from methanol (with active charcoal). It was subjected to purification by preparative thin layer chromatography on silica gel to give an analytical sample (Found: C, 70.64; H, 4.26; N, 11.38%. Calcd for $C_{22}H_{16}ClN_3O$: C, 70.69; H, 4.31; N, 11.24%), mp 182 °C (pale yellow); λ_{max} (ethanol) 259, 276(shoulder), and 369 nm (log ε=4.41, 4.35, and 3.64, respectively); ν_{max} (KBr) 3460, 3370, 1625, and 835 cm^{-1}; mass *m/e* 373(M^+, 19%) and 105(100); NMR ($CDCl_3$) τ 5.62(broad singlet, 2H, NH), 2.38—2.90(multiplet, 12H, aryl H), and 1.60(multiplet, 2H, aryl H). The later fraction gave 80 mg (12%) of compound VIII as white crystals on recrystallization from benzene, mp 217—218 °C, whose IR spectrum was identical with that of the product obtained by hydrogenation of compound IIa.

*Nitration of Compound IIa. 2,5-Bis-(*p*-chlorophenyl)-3,6-bis-(*p*-nitrophenyl)-1,2,4,5-tetra-azapentalene (IId)*: Nitric acid (0.33 ml, d=1.38) was added to a solution of compound IIa (1.0 g) in 11 ml of concentrated sulphuric acid. The mixture was stirred for 10 hr at room temperature and poured onto 200 ml of ice water. The yellow solid was collected, washed thoroughly with water, and dried to yield 1.27 g of a dinitro compound. Recrystallization from acetone gave a pure specimen (Found: C, 59.34; H, 2.92; N, 13.95%. Calcd for $C_{28}H_{16}Cl_2N_6O_4$: C, 58.86; H, 2.82; N, 14.71%), mp> 365 °C, whose IR spectrum was identical with that of compound IId, prepared by dimerization of 4-(*p*-chlorophenylazoethynyl)nitrobenzene.

*Bromination of Compound IIa. 3,6-Bis-(*p*-bromophenyl)-2,5-bis-(*p*-chlorophenyl)-1,2,4,5-tetra-azapentalene (IIe) and 3-*p*-Bromophenyl-2,5-bis(*p*-chlorophenyl)-6-phenyl-1,2,4,5-tetra-azapentalene (XII)*: Bromine (0.19 g) in 31 ml of chloroform was added with stirring to a solution of compound IIa (0.29 g) in 20 ml of chloroform, and the mixture was allowed to stand overnight. It was then heated under reflux for 15 min to complete the reaction. After cooling, it was washed with aqueous sodium thiosulphate solution to remove excess of bromine. The organic layer was dried over anhydrous sodium sulphate, and the solvent was removed by distillation to yield 0.3 g of yellow solid. A part of the solid (10 mg) was subjected to preparative thin layer chromatography on silica gel in benzene. The first, the second, and the third bands were scraped off the plate and extracted with dichloromethane and evaporation of the extracts gave 0.8 mg (6%) of the dibromine, 4.3 mg (38%) of the monobromide, and 4.7 mg of the starting material, respectively. The dibromide, mp 349 °C, was identified with IIe by mixed melting point and comparison of its IR spectrum with that of an authentic sample. The monobromide (XII) (Found: C, 56.58; H, 3.05; N, 10.74%. Calcd for $C_{24}H_{17}BrCl_2N_4$: C, 56.28; H, 3.25; N, 10.94%) showed mp 294.5—295.5 °C (yellow needles); ν_{max} (KBr) 1515, 1485, 1465, 1400, 1340, 1190, 1160, 1010, 965, 840, 760, and 675 cm^{-1}.

References

1) The parent structure may be named 2*H*,5*H*-pyrazolo-[4,3-*c*] pyrazole.
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