with 300 ml. of ether and 150 ml. of water, the ethereal layer was dried over sodium sulfate, concentrated and crystallization induced by the addition of petroleum ether (b.p. $35-65^{\circ}$). The acid (XXIIb), 2.88 g., m.p. 126-146°, after softening at 105°, appeared to be solvated.

An additional 0.73 g. of acid, m.p. $125-135^{\circ}$, softening at 105° , was obtained from the aqueous phase by continuous extraction with ether. The yield of acid was 70%.

The acid crystallized from acetone-benzene in fine white needles which softened at 142° and melted clear at 147°.

Anal. Calcd. for $C_{10}H_9O_3N$: C, 62.82; H, 4.74; N, 7.32. Found: C, 63.03; H, 4.89; N, 6.98.

That XXIIb is not immediately rearranged to 2-oxo-1,2,3,4-tetrahydroquinoline-4-carboxylic acid (VI) is indicated by the fact that only the acetic acid (XXIIb) was recovered from an aqueous solution at ρ H 1 after being kept at 30° for 15 hours. However, refluxing XXIIIb for 30 minutes in 6% hydrochloric acid effected rearrangement to VI, m.p. 218°.

CHICAGO, ILL.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY COLLEGE, CORK, IRELAND]

Polynitrogen Systems from Hydrazinocarbonic Acids. I. Diformazans¹

By F. L. Scott, ^{1a} D. A. O'Sullivan and J. Reilly

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The formation of iminotricarbaundecaztetraenes from dialdehydic diaminoguanidines and the oxidation of the resulting formazans have been discussed. Here, the main points of interest are the ready symmetrical fission of the new diformazan system on oxidation, and the specificity of its mode of formation. A number of additional new formazan systems derived from tetrazolyl- and quinolylhydrazones as starting substances are described. The preparation of some new guanazyls is given, chiefly as a comparison with the other couplings.

Coupling of an aldehydic hydrazone (R—CH== N^{α}·NH^{β}R') with an electrophilic² diazonium cation (Dn⁺) may result in one of three possible modes of attack: (i) reaction of Dn⁺ with the β -nitrogen atom—with tetrazene formation³; (ii) reaction of the electrophile with R or R'⁴; or (iii) by reaction of the Dn⁺ with the methine carbon to yield a formazan.⁵

Competitive reaction occurs, the center of highest electron density having the greatest likelihood of combination with Dn⁺. To enhance the possibility of formazan formation (the process of interest, in the present work), the nucleophilicity of the other possible reaction centers must be diminished. R is already deactivated by conjugation with the methine unsaturation, and, in the present experiments where R was always aromatic, it was occasionally further deactivated by nitrosubstitution. If R were aromatic it would be activated by its bonding to the (unprotonized) β -nitrogen atom. To eliminate this possibility, in the present series, only hydrazones were examined where R' was both aliphatic and electrophilic. This last quality in this radical also diminished the possibility of tetrazene formation. Thus attention was confined to aryl aldehydic derivatives of the hydrazinocarbonic acid class.

The coupling reactions of the guanylhydrazones, previously⁶ investigated, were in accord with these

(1) Previous preliminary notes on this topic from this laboratory have been: F. L. Scott, D. A. O'Sullivan and J. Reilly, J. Chem. Soc., 3508 (1951); Chem. and Ind., 782 (1952).

(1a) Chemistry Department, University of California, Los Angeles, 24, Calif.

(2) C. R. Hauser and D. S. Breslow, THIS JOURNAL, 63, 418 (1941).
(3) (a) Busch (and co-workers) postulate that tetrazene coupling is a preliminary to formazan formation. See for example M. Busch and H. Pfeiffer, Ber., 59, 1162 (1926); M. Busch and R. Schmidt, *ibid.*, 63B, 1950 (1980); J. prakt. Chem., (II), 131, 182 (1931); compare (b) K. A. Hofmann and H. Hock, Ber., 44, 2946 (1911).

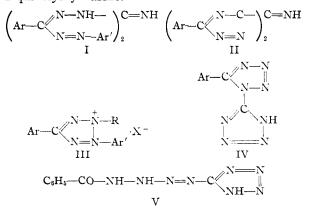
(4) I. Hauser, D. Jerchel and R. Kuhn, Chem. Ber., 84, 651 (1951). Compare also W. E. Bachmann and R. A. Hoffmann, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 224.

(5) H. von Pechmann, Ber., 27, 1690 (1894).

(6) E. Wedekind, Ber., 30, 444 (1897).

expectations—formazans or "guanazyls" being formed very readily. This present communication extends the investigation to some diaminoguanidine derivatives and demonstrates the analogy with the monoaminoguanidine compounds. Despite this, however, aldehydic acylhydrazones do not, in general, afford formazans.⁷

In addition to determining the relative coupling efficiency of dialdehydic diaminoguanidines, with the synthesis of a new formazan system, the 6-imino-1,3,9,11-tetraaryl-3,6,9-tricarbaundecaz-1,3,8,10tetraene (I), the present experiments were designed to provide a new tetrazole type—the bis-(5-aryl-2'-tetrazolyl)-formimine (II) class. The formation of the congeners of the iminotricarbaundecaztetraenes proved specific, and a qualitative comparison system was developed. The standard reference substances were benzaldehyde phenylhydrazone and benzaldehyde guanylhydrazone. Comparison was also made with the derivatives of the heterocyclic hydrazines, 5-hydrazinotetrazole and 2-quinolylhydrazine.



The phenyldiazonium ion reacted readily with benzaldiaminoguanidine and with benzal-2-quinolylhydrazine, in line with the ready reaction of this

⁽⁷⁾ Vide F. L. Scott, M. Ruszkiewicz and J. Reilly (forthcoming publication).

		_					-Analy	ses, %-		
Aldehyde	Hydrazine	Form identifiedª	Formula	М.р., °С.	cC	alculat H	ed N	с	Found H	N
Anisaldehyde	Aminoguanidine ^b	Picrate	$\mathrm{C_{15}H_{15}N_{7}O_{8}}$	250	••	.	23.2	••		23.2
Piperonal	Aminoguanidine ^b	Free base [°]	$C_9H_{10}N_4O_2$	184	48.2	5.3	25.6	48.3	5.1	24.6
Δ^{3} -Cyclohexylaldehyde	Aminoguanidine ^b	Nitrate	$C_8H_{15}N_5O_3$	129	41.9	6.5	30.5	41.9	6.8	30.2
Δ^3 -Cyclohexylaldehyde	Aminoguanidine ^{b}	Picrate	C14H17N7O7	216			24.8	••		24.6
Anisaldehyde	$Diaminoguanidine^b$	Free base'	$C_{17}H_{19}N_5O_2$	166	59.4	6.1	20.4	59.8	5.9	20.2
Cuminic aldehyde	Diaminoguanidine ^b	Nitrate	$C_{21}H_{28}N_6O_3$	145	• •		20.4			20.4
Δ^3 -Cyclohexylaldehyde	Diaminoguanidine ^b	Picrate	$C_{1}H_{28}N_8O_7$	202	50.2	5.1	22.3	50.2	5.1	23.0
o-Nitrobenzaldehyde	Diaminoguanidine ^b	Nitrate	$C_{16}H_{14}N_8O_7$	244	43.1	3.4	26.8	42.9	3.5	26.9
p-Nitrobenzaldehyde	Diaminoguanidine ^b	Nitrate	$C_{15}H_{14}N_8O_7$	187	43.1	3.4	26.8	42.2	3,3	26.2
<i>m</i> -Nitrobenzaldehyde	2-Quinolylhydrazine	Free base	$C_{16}H_{12}N_4O_2$	212	65.7	4.1	19.2	65.6	3.8	19.3

TABLE I Some Hydrazone Derivatives

^a These derivatives are either new substances or represent supplementary derivatives of previously described parent substances. ^b Reacted as nitrate. ^c Analysis corresponds to a monohydrate.

ion with benzaldehyde phenylhydrazone and -guanylhydrazone. The diazonium salts of sulfanilic acid, o-nitroaniline, o-nitrotoluidine, β -naphthylamine, p-nitroaniline and 4-chloro-o-toluidine also coupled with benzaldiaminoguanidine, while mnitrobenzaldiaminoguanidine coupled with both diazotized aniline and m-nitroaniline. With heterocyclic diazonium salts specificity was evident. Thus, while benzaldiaminoguanidine coupled with diazotized 4-aminoantipyrine it did not react with 5-tetrazolyl-, 2-thiazolyl- or 2-benzthiazolyldiazonium salts.

Similarly, benzaldehyde guanylhydrazone resisted coupling with heterocyclic diazonium salts (reacting only with diazotized 5-aminotetrazole^{3b}) while the anisaldehyde and 2,3,5,6-tetrahydrobenzaldehydeguanylhydrazones also coupled readily with 5-diazotetrazole. Anisaldehydequinolylhydrazone coupled with phenyldiazonium chloride but was unreactive toward the tetrazolyldiazonium salt.

Formazans, in general, are readily oxidized initially to tetrazolium salts (III) and then to tetrazoles. In this latter step either R or Ar' (vide III) has to be eliminated. The guanazyls oxidize by elimination of the guanyl group.⁸

Analogously, the iminotricarbaundecaztetraenes were now also found to be readily oxidized. With lead tetraacetate, or nitrous oxide in chloroform, they yielded the corresponding monotetrazoles in place of the possible ditetrazoles (II). With concentrated nitric acid, nitrated monotetrazoles similarly resulted, *e.g.*, 6-imino-1,3,9,11-tetraphenyl-3,6,9-tricarbaundecaz-1,3,8,10-tetraene gives a mixture of isomeric dinitrodiphenyltetrazoles, and 6imino-1,11-di-*p*-nitrophenyl-3,9-diphenyl-3,6,9-tricarbaundecaz-1,3,8,10-tetraene also gave a dinitrodiphenyltetrazole.

Finally, as a cognate investigation, efforts were made to synthesize a further 1,5'-ditetrazole (IV) system by the alkali cyclization of 1-benzoyl-4tetrazolylisotetrazene (V). The initial high-yield reaction product split into the corresponding benzamide and a tetrazolyl fragment after this treatment. In the presence of alkali⁹ the tetrazene formed preferentially underwent fission rather than cyclization.

Experimental^{10,11}

Hydrazone Formation.—The guanyl- and quinolylhydrazones and the dialdehydic diaminoguanidines were prepared by refluxing the calculated quantities of aldehyde and hydrazine for a few moments in aqueous ethanolic solution. The free bases of the guanylhydrazones were isolated without isolating the nitrate but this resulted in some decomposition in the case of the diaminoguanidine compounds and separation of the intermediate salt was usually effected. The properties of some of the hydrazones concerned are summaized in Table I.

Formazan Formation.—Couplings were performed as previously described¹; isolation of the formazan was effected by either pouring the pyridine solution into dilute hydrochloric acid solution or by dilution with water, and, if no precipitation resulted, extraction with chloroform. The chloroform solution usually deposited a tar, but on working up the dye could be isolated. A typical example of the general formazan technique is as follows.

 $0.\bar{0}1$ mole of finely powdered benzylidene-5-hydrazinotetrazole was added to a large excess (100 ml.) of 5% sodium hydroxide solution. The yellow solution which resulted was cooled to 5° and added to 0.01 mole of diazotized aniline. Immediately a deep-red color was produced and a very small amount of solid precipitated. The filtrate on neutralization with dilute acetic acid yielded a solid which, while proving only slightly soluble in water was fairly soluble in ethanol; total yield 50–60%. On careful recrystallization from ethanol-water a solid melting at 147° was obtained which was proved by analysis to be 1,3-diphenyl-5-tetrazolyl-3-monocarbapentaz-1,3-diene.

Anal. Caled. for $C_{14}H_{12}N_8$: C, 57.5; H, 4.1; N, 38.3. Found: C, 57.7; H, 4.2; N, 38.2.

The properties of the other formazans are summarized in Table II.

Oxidation of the Formazans.—A number of different techniques were employed—concentrated nitric acid, nitrous oxide or lead tetraacetate in chloroform and finally dilute aqueous nitric acid.

(a) Three and one-half grams (0.01 mole) of finely powdered 6-imino-3,6,9-tricarbaundecaz-1,3,8,10-tetraene was added cautiously to 130 ml. of concentrated nitric acid. Even at room temperature a very gentle agitation initiated a vigorous reaction with copious evolution of nitrous fumes. After refluxing gently for 1.25 hours the mixture was allowed to stand at room temperature for several hours when a yellow solid separated. It was filtered off and washed thoroughly with boiling water to remove any soluble impurities. After a final recrystallization from nitric acid, colorless plates melting at 198° were obtained. The analysis suggests this compound was a dinitrodiphenyltetrazole.

Anal. Caled. for $C_{13}H_8N_6O_4$: C, 50.0; H, 2.9; N, 26.9. Found: C, 50.1; H, 2.9; N, 26.9.

Addition of water to the filtrate yielded a further precipitate of an orange-colored solid, which on recrystallization from aqueous ethanol had a m.p. of 154° . This proved similarly to be an isomeric dinitrodiphenyltetrazole.

⁽⁸⁾ Compare the ready hydrolysis of 1-guanylpyrazoles, F. L. Scott and J. Reilly, THIS JOURNAL, **74**, 4563 (1952).

⁽⁹⁾ Cf. O. Dimroth and G. de Montmollin, Ber., 43, 2907 (1910).

⁽¹⁰⁾ All m.p.'s are uncorrected.

⁽¹¹⁾ All analyses are by Drs. Weiler and Strauss, Oxford, England.

FORMAZANS $\left(Ar - C \left\langle N - NH - M \right\rangle_{n} \right)_{n}$

HydraonaDisorded uniceArReacting (A)Reacting (A)Point (A)<				-		u							2			
Hytanone Diractised antiles Ar Resting product model C, Hi NO, L Formula Model C Model C Model C Hi NO, L HS F/5 B 15 F/5 C, H C/H, NO C H B S/5 L L B F/5 B F/5 H B F/5 H B F/5 H B B B B									t	ľ	Salcula	1 3	lyses, %	Found	I with the	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Hydrazone	Diazotized amine ^a		Reaction product- Ar'		(=	Formula	М.р., °С. ^b	Coup- ling mode	C	н	N" (or halo- gen)	с	н	N° (or halo- gen)	
maylidenediaminoguanidine p.Nitroaniline C ₄ H ₃ C ₄ H ₄ NO ₇ P >C=NH 2 C ₇ H ₁ N ₁ O ₁ 175 A 57.5 3.7 57. and 57.5 3.7 56. arylidenediaminoguanidine p.Nitrotoluidine C ₄ H ₃ C ₄ H ₄ NO ₇ P >C=NH 2 C ₂ H ₂ N ₁ O ₁ 175 A 57.5 3.7 56. arylidenediaminoguanidine p.Nitrotoluidine C ₄ H ₃ C ₄ H ₄ NO ₇ P >C=NH 2 C ₂ H ₂ N ₁ O ₁ 108 B 58.9 5.2 50. arylidenediaminoguanidine p.Nitrotoluidine C ₄ H ₃ C ₄ H ₄ NO ₇ P >C=NH 2 C ₂ H ₂ N ₁ O ₁ 108 B 58.9 5.2 50. arylidenediaminoguanidine f.Nitrotoluidine C ₄ H ₃ C ₄ H ₄ N ₁ O ₁ > C=NH 2 C ₂ H ₂ N ₁ O ₁ 161 114 4 22.1 61. arylidenediaminoguanidine f.Aminoartipyrine C ₄ H ₃ C ₁ H ₄ N ₁ O ₄ >C=NH 2 C ₂ H ₂ N ₁ O ₁ 154 A 64.1 5.1 26.3 64. arylidenediaminoguanidine 5.Aminotetrazole C ₄ H ₃ C ₁ H ₄ N ₁ O ₄ >C=NH 2 C ₂ H ₂ N ₁ O ₁ 160 149 ⁶ C 38.6 5.7 45.8 c 45.	enzylidenediaminoguanidine		C ₆ H ₆	C6H4-NO2-0	>C=NH	-	$C_{27}H_{21}N_{11}O_4$	115	в	57.5	3.7	:	57.5	4.0	÷	
enzylidenediaminoguanidine o-Nitrotohudine C ₄ H ₃ $C_{4H_3}^{(H_4)}$ >C=NH 2 C ₃ H ₃₈ N ₁ O ⁴ 94 B 55.8 4.0 56. Enzylidenediaminoguanidine o-Nitrotohudine C ₄ H ₃ $C_{4H_3}^{(H_4)}$ >C=NH 2 C ₄ H ₃₇ N ₁ O ⁴ 108 B 58.9 5.2 50. Enzylidenediaminoguanidine β -Naphthylamine C ₄ H ₃ $C_{4H_3}^{(H_4)}$ >C=NH 2 C ₄ H ₃₇ N ₁ O ₄ 108 B 58.9 5.2 50. Enzylidenediaminoguanidine β -Chloro-2-tohudine C ₄ H ₃ $C_{4H_4}^{(H_4)}$ >C=NH 2 C ₄ H ₃₇ N ₁ O ₄ 163 A 73.3 4.7 21.9 73. Enzylidenediaminoguanidine β -Chloro-2-tohudine C ₄ H ₃ $C_{4H_4}^{(H_4)}$ = C ₄ H ₄ N ₁ O ₄ 2 C_{3} H ₃₅ N ₅ U ₄ 63 B 61.1 4.4 22.1 61. Enzylidenediaminoguanidine β -Aminotetrazole C ₄ H ₃ $C_{4H_4}^{(H_4)}$ = C ₆ M ₁ H ₃ 1 $C_{4H_4}^{(H_4)}$ = 2 $C_{4H_4}^{(H_4)}$ 1 $C_{4H_4}^{(H_4)}$ 1 2 H_{4} N ₁ O ₄ 1 1 4 2 .1 $61.$ Evylideneaminoguanidine β -Aminotetrazole C ₄ H ₄ C H ₇ β $-C_{7}^{(H_4)}$ 1 $C_{4H_4}^{(H_4)}$ 1 1 $G_{4H_4}^{(H_4)}$ 1 2 H_{4} N ₁ O ₄ 1 1 4 2 .1 $61.$ 1 1 1 1 1 1 1 1 1 1	enzylidenediaminoguanidine		C ₆ H ₆	$C_6H_4 \cdot NO_{2-}p$	>C=NH		C₂rH₂ıN⊔O₁	175	A	57.5	3.7	:	57.4	3.6	÷	
enzylidenediaminoguanidine e -Nitrotoluidine C_{4H_3} C_{4H_7} V_{Orro} > C=NH 2 $C_{3H_2N_1Or}$ 108 B 58.9 5.2 50. enzylidenediaminoguanidine β -Naphthylamine C_{4H_3} C_{4H_7} V_{Orro} > C=NH 2 $C_{3H_2N_1O_7}$ 168 B 58.9 5.2 50. enzylidenediaminoguanidine β -Choro-2-toluidine C_{4H_3} C_{4H_4} V_{CH_2} > C=NH 2 $C_{3H_2N_1O_7}$ 159 73. 4.7 21.9 73. enzylidenediaminoguanidine β -Choro-2-toluidine C_{4H_3} C_{4H_4} V_{CH_4} > C=NH 2 $C_{3H_3N_1O_7}$ 159 β 64.1 5.1 26.3 64. enzylidenediaminoguanidine β -Aminotetrazole C_{4H_4} C_{1H_4} $C_{1H_4N_1O_4}$ 12.44 22.1 61. enzylidenediaminoguanidine β -Aminotetrazole C_{4H_4} C_{1H_3} $C_{1H_4N_1O_4}$ 149 ^A C 38.6 5.7 30. enzylideneaminoguanidine β -Aminotetrazole C_{4H_4} P_{CH_7} $-C_{NH_4}^{NH_4}$ 1 $C_{3H_4N_1O_4}$ 149 ^A C 38.6 5.7 45.8 M_{12} free ieraminoguanidine β -Aminotetrazole C_{4H_4} P_{7P_7} CHN_75 $-C_{NH_4}^{NH_4}$ 1 $C_{3H_4N_1O_4}$ 149 ^A C 38.6 5.7 45.8 M_{12} free ieraminoguanidine β -Aminotetrazole C_{4H_4} P_{7P_2} CHN_75 $-C_{NH_4}^{NH_4}$ 1 $C_{3H_4N_1O_4}$ 149 ^A C 38.6 5.7 45.8 M_{12} free ieraminoguanidine β -Aminotetrazole C_{4H_4} P_{7P_2} CHN_75 $-C_{NH_4}^{NH_4}$ 1 $C_{3H_4N_1O_4}$ 149 ^A C 38.6 5.7 45.8 M_{12} free ieraminoguanidine β -Aminotetrazole C_{4H_4} P_{7P_2} CHN_75 $-C_{NH_4}^{NH_4}$ 1 $C_{3H_4N_1O_4}$ 149 ^A C 38.6 5.7 45.8 M_{12} free ieraminoguanidine β -Aminotetrazole C_{4H_4} P_{7P_2} M_{12}	enzylidenediaminoguanidine	o-Nitrotoluidine	C ₆ H ₅	\sim	>C==NH		C29H25N11O4	94	B	55.8	4.0	•	55.7	4.3	:	
enzylidenediaminoguanidine β -Naphthylamine C_{aH_3} $C_{aH_7}\beta$ >C=nH 2 $C_{aH_3}N_3C_{12}$ i_{63} A 73.3 4.7 21.9 73. enzylidenediaminoguanidine 4 -Chloro-2-toluidine C_{aH_3} $C_{aH_1}C_{CL_4}$ >C=nH 2 $C_{aH_3}N_3C_{12}$ i_{54} A $i_{64.1}$ j_{-1} $i_{22.3}$ $i_{64.1}$ $i_{64.1}$ $i_{64.1}$ $j_{64.1}$ $j_{64.1}$ $j_{64.1}$ $i_{64.1}$ $j_{64.1}$ j	enzylidenediaminoguanidine	o-Nitrotoluidine	C,H,	\setminus /	>C=NH		C21H25N11O4	108	в	58.9	5.2	:	59.2	5.0	•	
emzylidenediaminoguanidine 4-Chloro-2-toluidine CaHs CaHs $C_{aHs} \rightarrow C=NH$ 2 $C_{aHs}N_{aO}C_{b}$ 63 B 61.1 4.4 22.1 61. enzylidenediaminoguanidine 4-Aminoantipyrine ⁶ CaHs $C_{aHs} \rightarrow C=NH$ 2 $C_{aHs}N_{aO}$ 154 A 64.1 5.1 26.3 64. rexylideneaminoguanidine 5-Aminotetrazole CaHs $C_{aHs} \rightarrow C=N_{Hs} \rightarrow C=N$	oenzylidenediaminoguanidine		C ₆ H ₅	С ₁₀ Н ₇ -β СH9	>C≔NH		$C_{35}H_{27}N_9$	163	V	73.3	4.7	21.9	73.8	4.8	22.2	
Senzylidenediaminogramidine4-Aminoantipyrine* C_{HI} $C_{HH}N_{10}$ 2 $C_{\pi H_3}N_{10}O_{\pi}$ 154^{h} A 64.1 5.1 26.3 64.1 hexylideneaminogramidine 5 -Aminotetrazole C_{4H_1} $C_{1H_1}O_{\pi}$ 1 $C_{4H_4}N_{10}$ 149^{h} C 38.6 5.7 38.6 57 39.6 meaminogramidine 5 -Aminotetrazole $C_{4H_4}OCH_{\pi}F$ $CHN_{\pi}-5$ $-Cennet NH_2$ 1 $C_{10}H_{13}N_{10}O$ 146^{h} C 38.6 57 39.6 meaminogramidine 5 -Aminotetrazole $C_{4H_4}OCH_{\pi}F$ $-Cennet NH_2$ 1 $C_{10}H_{13}N_{10}O$ 146^{h} C 38.6 57 39.6 feleneaminoguanidine 5 -Aminotetrazole $C_{4H_4}OCH_{\pi}F$ $-Cennet NH_2$ 1 $C_{10}H_{13}N_{10}O$ 146^{h} C 38.6 57 39.6 benzylideneaminoguanidine 5 -Aminotetrazole $C_{4H_4}CH_FF$ $CHN_{\pi}F5$ $-Cennet NH_2$ 1 $C_{10}H_{18}N_{10}O$ 146^{h} C 31.8 31.6 3	oenzylidenediaminoguanidine	4-Chloro-2-toluidine	0	\setminus \angle	>C=NH		C29H25N9Cl2	63	В	61.1	4.4	22.1	61.0	4.8	21.8	
hexylideneaminoguanidine 5-Aminotetrazole C_6H_{10} CHN_r5 $-C_{MH_2}$ $I_{c_9H_1M_{10}}$ I_{49}^{h} $C_{38.6}$ 5.7 30. reaminoguanidine 5-Aminotetrazole C_6H_4 . PCH_r5 $-C_{MH_2}$ $I_{c_1}C_{H_1SN_10}$ I_{49}^{h} $C_{38.6}$ 5.7 45.8' 47 ideneaminoguanidine 5-Aminotetrazole C_6H_4 . PCH_r5 $-C_{MH_2}$ $I_{c_1}C_{H_1SN_10}$ I_{46}^{h} C_{11} 45.8' 47 benzylideneaminoguanidine 5-Aminotetrazole C_6H_4 . PCH_r5 $-C_{MH_2}$ $I_{c_2}H_{16}N_{10}$ I_{28} $A_{48.0}$ 5.3 47 benzylideneaminoguanidine 5-Aminotetrazole C_6H_4 . CL_1 C_{HN_r5} $-C_{MH_2}$ $I_{c_2}H_{16}N_{10}$ I_{28} $A_{48.0}$ 5.3 47 benzylideneaminoguanidine 5-Aminotetrazole C_{6H_5} C_{H} $C_{HN_{12}5}$ $-C_{MH_2}^{NH_2}$ $I_{c_2}H_{16}N_{10}$ I_{28} $A_{48.0}$ 5.3 47 ene-2-quinolylhydrazine Aniline C_{6H_5} C_{H} C_{H_6} C_{H_6} V_{1H_2} I_{c_2} V_{1H_2} I_{c_2} I_{c_3} I_{11} A_{12} I_{c_3} I_{H_2} I_{c_3} I_{c_3	benzylidenediaminoguanidinc	4-Aminoantipyrine ^o	C ₆ H ₅	C ₁₁ H ₁₁ N ₃ O-4	>C=NH		C37H35N13O2	154 ^h	Α	64.1	5.1	26.3	64.5	5.2	25.8	
The aminogranidite 5-Aminotetrazole $C_{\theta}H_4 \cdot OCH_3 - p$ $CHN_4 - 5$ $-C_{NH_3}^{OH_4}$ $1 C_{10}H_{12}N_{10}O$ 146^{h} C \dots 45.8' M_7 idencaminoguanidine 5-Aminotetrazole $C_{\theta}H_4 \cdot Pr^{\mu}-p$ $CHN_4 - 5$ $-C_{NH_3}^{OH_4}$ $1 C_{12}H_{16}N_{10}$ 128 A 48.0 5.3 \dots 47 beazylideneaminoguanidine 5-Aminotetrazole $C_{\theta}H_4 \cdot Pr^{\mu}-p$ $CHN_4 - 5$ $-C_{NH_3}^{OH_4}$ $1 C_{12}H_{16}N_{10}$ 128 A 48.0 5.3 \dots 47 beazylideneaminoguanidine 5-Aminotetrazole $C_{\theta}H_4 \cdot C-H_{16}$ $C_{HN_4}^{OH_4}$ $1 C_{12}H_{16}N_{10}$ 128 A 48.0 5.3 \dots 47 beazylideneaminoguanidine 5-Aminotetrazole $C_{\theta}H_4 \cdot CL-p$ $CHN_4 - 5$ $-C_{NH_3}^{OH_4}$ $1 C_{2}H_{16}N_{10}$ C_{11} 146 A 34.8 3.6 $C_{11} = 35$ ene-2-quinolylhydrazine Aniline $C_{\theta}H_3$ $C_{H_3}^{OH_4}$ $C_{9}H_6N_3(2)$ $1 \cdot C_{2}H_{17}N_3$ 160 A 75.2 4.8 20.0 74 shares to the methods of diazotization employed, see K. H. Saunderg, "The Aromatic Diazo Compounds," Arold & C_{0}. London, 1949. ^b Melting t share. They usually occurred with preliminary loss of volume and with decomposition. ^e Mode A represents the procedure: ethanolic solution of hycalium salt solution. Mode B represents pyridine solution. ^e Mode A represents the procedure: ethanolic solution of hycalenes the sectio adja solution of hydrazone + solution. Mode B represents pyridine solution of hydrazone + Solution solution for diazotive scoresponds to the anhydrous form and is isolated in a different manner. ^e N, N-Dibenzylidened ouple, by either methods A or B, with diazotized 2-aminothiazole, 2-aminobenzthiazole or 5-aminotetrazole. ^A Analysis corresponds to a monohydrate. ¹ 0.1. ^k Found for MeO, 10.4.	hexylideneaminoguanidine	5-Aminotetrazole	C ₆ H ₁₀	CHN4-5	-C	1	C9H14N10	149 ⁴	c	38.6	5.7	÷	39.2	6.0	:	
ideneaminoguanidine 5-Aminotetrazole $C_6H_4 \cdot Pr^{\beta}-p$ CHN_4-5 $-C_{NH_3}^{MH_4}$ 1 $C_{19}H_{16}N_{10}$ 128 A 48.0 5.3 47 benzylideneaminoguanidine 5-Aminotetrazole $C_6H_4 \cdot Cl^-p$ CHN_4-5 $-C_{NH_3}^{M}$ 1 $C_{19}H_9N_{10}Cl$ 146 A 34.8 3.6 $Cl = 35$ ene-2-quinolylhydrazine Aniline 5 -Aminotetrazole C_6H_5 C_6H_6 $C_{9H_6}N_3(2)$ 1 $C_{22}H_1N_5$ 160 A 75.2 4.8 20.0 74 efferences to the methods of diazotization employed, see K. H. Saunders, "The Aromatic Diazo Compounds," Arnold & Co., London, 1949. ^b Melting 1 sharp. They usually occurred with preliminary loss of volume and with decomposition. ^c Mode A represents the procedure: ethanolic solution of hy solute actic acid solution of hydrazone + solutum actate + aqueous diazonium salt solution of hydrazone + [solutum carbonate ethanolic solution of diazoniu solute. ^c Analysis corresponds to a dihydrate. ^c This corresponds to the anhydrous form and is isolated in a different manner. ^e N,N'-Dibenzylidened ouple, by either methods A or B, with diazotized 2-aminothiazole, 2-aminobenzthiazole or 5-aminotetrazole. ^A Analysis corresponds to a monohydrate.	neaminoguanidine	5-Aminotetrazole	C ₆ H ₄ ·OCH ₃ - <i>p</i>	CHN4-5	-CANH NH ₂	н	C ₁₀ H ₁₂ N ₁₀ O	146 ^h	с С	:	:	45.8 <i>i</i>	:	:	45.0^{k}	
benzylideneaminoguanidine 5-Aminotetrazole $C_{6}H_{4}$ ·Cl- p CHN ₄ -5 $-C$ NH_{2} 1 $C_{9}H_{9}N_{10}$ Cl 146 A 34.8 3.6 Cl = 35 11.4 ene-2-quinolylhydrazine Aniline $C_{6}H_{5}$ $C_{6}H_{6}$ $C_{9}H_{6}N_{3}(2)$ 1 $C_{2}H_{9}N_{10}$ Cl 146 A 75.2 4.8 20.0 74 efferences to the methods of diazotization employed, see K. H. Saunderg, "The Aromatic Diazo Compounds," Arnold & Co., London, 1949. 6 Melting 1 sharp. They usually occurred with preliminary loss of volume and with decomposition. 6 Mode A represents the procedure: ethanolic solution of hyveolium hydroxide + diazonium salt solution. Mode B represents pyridine solution of hydrazone + [sodium carbonate neutralized] solution of diazoniu s dilute acctic acid solution in the according to the analysis corresponds to a dilydrazone + [sodium carbonate neutralized] solution of diazoniu s dilute actic acid solution is soluted to the analysis corresponds to a dilydrazone in this corresponds to the anhydrous form and is isolated in a different manner. 6 N,N'-Dibenzylidened ouple, by either methods A or B, with diazotized 2-aminobenzthiazole or 5-aminotetrazole. A Analysis corresponds to a monohydrate. 10.1. ⁴ Found for MeO, 10.4.	ideneaminoguanidine	5-Aminotetrazole	C ₆ H ₄ ·Pr ^A -p	CHN4-5	-C NH3 NH3	-	C12H16N10	128	V	48.0			47.9	6.2	• •	
ene-2-quinolylhydrazine Aniline $C_{6}H_{5}$ $C_{6}H_{6}$ $C_{9}H_{6}N_{3}(2)$ 1 $C_{22}H_{17}N_{5}$ 160 A 75.2 4.8 20.0 74 efferences to the methods of diazotization employed, see K. H. Saunders, "The Aromatic Diazo Compounds," Arnold & Co., London, 1949. ^b Melting 1 sharp. They usually occurred with preliminary loss of volume and with decomposition. ^e Mode A represents the procedure: ethanolic solution of hyt sodium hydroxide + diazonium salt solution. Mode B represents pyridine solution of hydrazone + [sodium carbonate neutralized] solution of diazoniu s dilute acetic acid solution of hydrazone + sodium acetate + aqueous diazonium salt solution. ^d Except where otherwise expressed, the values in this values. ^e Analysis corresponds to a dihydrate. ^f This corresponds to the anhydrous form and is isolated in a different manner. ^e N,N'-Dibenzylidened ouple, by either methods A or B, with diazotized 2-aminothiazole, 2-aminobenzthiazole or 5-aminotetrazole. ^h Analysis corresponds to a monohydrate. ^{10,11} . ^k Found for MeO, 10.4.	benzylideneaminoguanidine	5-Aminotetrazole	C_6H_4 ·Cl- p	CHN4-5	\land /	1	C ₉ H ₉ N ₁₀ Cl	146	A	34.8		5H	35.2	3.6	Cl = 10.6	
eferences to the methods of diazotization employed, see K. H. Saunderg, "The Aromatic Diazo Compounds," Arnold & Co., London, 1949. ^b Melting I sharp. They usually occurred with preliminary loss of volume and with decomposition. ^e Mode A represents the procedure: ethanolic solution of hy solution hydroxide + diazonium salt solution. Mode B represents pyridine solution of hydrazone + [sodium carbonate neutralized] solution of diazoniu solution effect acid solution of hydrazone + solutina acetate + aqueous diazonium salt solution. ^a Except where otherwise expressed, the values in this ouple, by either methods to a dipydrate. ^J This corresponds to the anhydrous form and is isolated in a different manner. ^a N,N'-Dibenzylidened ouple, by either methods A or B, with diazotized 2-aminothiazole, 2-aminobenzthiazole or 5-aminotetrazole. ^b Analysis corresponds to a monohydrate. ^J 10.1. ^b Found for MeO, 10.4.	ene-2-quinolylhydrazine	Aniline	C ₆ H ₅	C ₆ H ₆	$C_9H_6N_2(2)$	-	$C_{22}H_{17}N_5$	160	Υ	75.2	4.8	20.0	74.5	4.9	20.5	
	eferences to the methods of d sharp. They usually occurris occurrity occurris solution bydroxide + diazoniu is dilute acetic acid solution of values. * Analysis correspond ouple, by cither methods A or ouple, by cither methods A or 10.1. * Found for MeO, 10.	liazotization employed ed with preliminary lo um salt solution. Moo di hydrazone + sodium ds to a dihydrate. 7 r B, with diazotized 2- 4.	, see K. H. Sau ss of volume and de B represents Lacetate + aque This corresponds aminothiazole, 2	nderg, "The Aro 1 with decompos pyridine solution cous diazonium s to the anhydroi 2-aminobenzthia	matic Diazo (sition. ^e Moć n of hydrazon salt solution. us form and i zole or 5-amir	Comple A le A d E; s isols notet	oounds," Arno represents the [sodium carbo where ot teed in a differ razole. ^A Ana	old & C proce onate n herwis lysis c	0., Lo dure: eutrali e expre nner. orrespe	ndon, ethanc zed] sc ssed, 1 ° N,1 onds to	1949. olic so olutior the va N'-Dil v'-Dil a mo	^b Melt dution o lution o lues in benzylid mohydr	ting poi of hydra conium this col flenediat ate. <i>i</i>	nts, ge vzone - salt. umn r minogi Anal.	enerally, + excess Mode C epresent uanidine Calcd.	

Anal. Caled. as above. Found: C, 49.8; H, 2.5; N, 26.3.

The yield of each solid was about 30%. Orientation of these substances by *ad hoc* syntheses has proved difficult and will be described subsequently. Similarly when 6-imino -3,9-di-p-nitrophenyl-1,11-diphenyl-3,6,9-tricar-baundecaz-1,3,8,10-tetraene and the 3,9-di-m-nitrophenyl analog were treated with concentrated nitric acid they reacted less vigorously than the 3,9-diphenyl compound, but after refluxing for 1-hour periods both yielded dinitrophenyl-tetrazoles of m.p. 190°.

(b) 8.86 g. (0.02 mole) of lead tetraacetate dissolved in chloroform was added to a solution of 3.5 g. (0.01 mole) of 6-imino-1,3,9,11-tetraphenyl-3,6,9-tricarbaundecaz-1,3,8,-10-tetraene in the same solvent. An immediate fading in color of the formazan solution resulted. The mixture was warmed gently for a few minutes before the chloroform was removed, under reduced pressure. The residue was taken up with 40 ml. absolute ethanol and all the lead precipitated by the passage of hydrochloric acid gas. Filtration, followed by thermal concentration resulted in the deposition of a white feathery material which on purification melted at $101.5-102^\circ$. Analysis showed this to be 2,5-diphenyl-tetrazole.

Anal. Calcd. for $C_{13}H_{10}O_4$: C, 70.3; H, 4.5; N, 25.2. Found: C, 70.2; H, 4.6; N, 24.4.

The yield was practically quantitative. The same reaction took place with nitrous oxide in chloroform solution. When 6-imino-3,9-diphenyl-1,11-o-nitro-p-tolyl-3,6,9-tricarbaundecaz-1,3,8,10-tetraene was oxidized by similar methods, 2-o-nitro-p-tolyl-5-phenyltetrazole of m.p. 101° was obtained.

Anal. Caled. for $C_{14}H_{11}N_{\delta}O_{2}$: C, 59.7; H, 3.9. Found: C, 59.0; H, 4.4.

(c) 0.005 mole of 6-imino-3-phenyl-1-tetrazolyl-3,6-dicarbaheptaz-1,3-diene was refluxed for 10 minutes with 60 ml. of 5% nitric acid. The resulting straw-yellow solution on filtering from suspended matter was neutralized with 5% sodium hydroxide and allowed to stand at 0° for 12 hours. A slight suspension of a gray material separated, was filtered off and was not further investigated. The remaining solution was thermally concentrated and the resulting organic solid separated from inorganic contaminants by extraction with a chloroform-ethanol mixture. On concentrating, a crystalline solid was precipitated which, after recrystallization from aqueous ethanol melted at 245–246°, yield was ca. 20%. The substance has an empirical formula of $C_9H_{10}N_6$.

Anal. Calcd. for $C_{3}H_{10}N_{6}$: C, 52.1; H, 4.8; N, 40.5. Found: C, 52.2; H, 4.9; N, 40.3.

A similar experiment using the anisylidene analog resulted in a solid of m.p. 265°. This also corresponds to a similar type empirical formula $C_{9}H_{9}N_{6}$ ·OCH₃. These are being further investigated.

Anal. Calcd. for $C_{10}H_{12}N_6O$: C, 51.6; H, 5.2; N, 36.2. Found: C, 51.8; H, 5.2; N, 36.2.

The use of the dilute acid increased the extent of hydrolysis and thus the evolution of the free aldehyde. This was an undesirable side reaction, but the use of the method was necessitated by the insolubility of the tetrazolylformazans in chloroform. Refluxing a pyridine solution of such formazans with permanganate to effect the oxidation afforded anomalous results.

Cyclization of a Tetrazolylisotetrazene.—On adding a solution of 0.01 mole of 5-tetrazolyldiazonium nitrate to a solution in the presence of excess sodium acetate solution, a white precipitate of crude 1-benzoyl-4-tetrazolyl-isotetrazene, m.p. $94-98^{\circ}$, 88% yield, separated immediately. As most purification techniques resulted in decomposition of the isotetrazene, it was subjected without purification to the cyclization technique of Dimroth and de Montmollin.⁸ Four and one-tenth grams of the well-powdered reaction product was added to 40 ml. of 5 N sodium hyroxide solution. An immediate yellow coloration took place. The suspension was agitated while the temperature was raised gently to 70° when ammonia vapor was given off. After filtration and subsequent crystallization from ethanol-water it was obtained as white crystals of m.p. 126° . It was shown to be benzamide by mixed melting point with an authentic sample and by analysis.

Anal. Calcd. for C₇H₇NO: C, 69.3; H, 5.8; N, 11.5. Found: C, 69.1; H, 5.7; N, 11.7.

Neutralization of the filtrate and extraction with ether made possible the recovery of a further yield of benzamide; total yield 20%. This experiment was repeated keeping the temperature of the alkaline suspension of tetrazene at 0° for 24 hours. Again benzamide was the main product recovered. The identification of the tetrazolyl fragment of the tetrazene fission was not pursued.

CORK, IRELAND

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

Steric Hindrance to Coplanarity in o-Fluorobenzidines^{1a,b}

By Andrew J. Bilbo and George M. Wyman Received June 15, 1953

2,2'-Difluoro-, 2,2',6,6'-tetrafluoro-, 2,2'-dichloro- and 3,3'-dichlorobenzidine were synthesized by standard methods and their ultraviolet absorption spectra measured. The spectra indicate that there is an appreciable inhibition of resonance in the *o*-halogenated benzidines, probably resulting from displacement of the molecule from a coplanar configuration. The bromine water tests observed for these molecules further support this theory.

Introduction

In conjunction with some work on conjugated polyphenyls, it was considered desirable to ascertain the steric interference with coplanarity caused by the introduction of fluorine atoms in the *o*positions in the biphenyl structure. In contrast with the corresponding alkyl and chlorine compounds, the *o*-tetrafluorinated derivatives of biphenyl have not been successfully resolved,² although a schematic drawing of the spatial ar-

(1) (a) The research reported in this paper was performed in part under the sponsorship of the Ordnance Corps, Department of the Army; (b) presented before the 124th Meeting of the American Chemical Society, Chicago, Ill., September, 1953.

(2) E. C. Kleiderer and R. Adams, THIS JOURNAL, 55, 4219 (1933).

rangement of atoms in such a molecule indicates the existence of considerable steric interference between the fluorine atoms on adjacent rings, as shown in Fig. 1. In order to accommodate these "overlapping" fluorine atoms in the limited space available between the two benzene rings, it is necessary for the phenyl groups to take up noncoplanar positions by twisting about the connecting 1,1'-bond until the steric interference is removed. Since the distance of closest approach in space between two adjacent fluorine atoms in organic molecules has been reported to be 2.70 Å.,³ the angle of torsion of the benzene rings can be calcu-

(3) H. P. Lemaire and R. L. Livingston, J. Chem. Phys., 18, 569 (1950).