The first drop in pressure corresponds to the disappearance of the phase of residual monomer by solution in the polymer. This occurs at about 52% conversion corresponding to a "solubility" of 0.92 g. of butadiene per g. of polybutadiene. This solubility is approximately the same at 30 and at 50°, and is unaffected by a sixteen-fold variation in the amount of soap used in preparing the emulsion charges. Equilibrium as regards distribution of monomer between the oil phase and the polymer phase appears to be maintained during the polymerization at 50°.

During the emulsion copolymerization of butadiene–styrene, the pressure changes continuously from the start of the reaction because of the change in the composition of the copolymer which is formed. At about 50–52% conversion a fairly abrupt drop in pressure occurs corresponding to the solution of excess monomers. The composition of the oil phase corresponds closely to the composition of the total residual monomers, which indicates that only a small change in composition of a butadiene–styrene mixture results from its distribution between the polymer and the oil phase.

MINNEAPOLIS, MINNESOTA RECEIVED AUGUST 16, 1948

[CONTRIBUTION FROM HOWARD UNIVERSITY]

Absorption Spectra of Azines and Dianils[1]

BY LLOYD N. FERGUSON AND THOMAS C. GOODWIN[2]

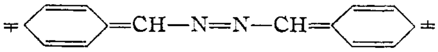
The order of increasing chromophoric power of the common chromophores was early recognized to be

$$C{=}C \quad C{=}N \quad C{=}O \quad N{=}N \quad C{=}S$$

This order has been attributed by several persons[3,4,5,6,6a] to the relative amounts of strain[7] within the double bonds. Other factors being equal, with increasing strain within the bond there results a less stable ground state, causing a smaller difference in the potential energies of the ground and first excited states and, hence, an absorption of light of longer wave length.

What appears to be at first glance an anomaly to this generalization is the fact that azines, which contain two stronger chromophores than a polyene hydrocarbon containing the same number of double bonds, absorb light of shorter wave length than the latter compounds. For instance, Lewis and Calvin[3] have pointed out that benzalazine, $C_6H_5CH{=}N{-}N{=}CHC_6H_5$, ($\lambda_{\text{max.}} = 301$ mμ) absorbs light at shorter wave lengths than does 1,4-diphenylbutadiene, $C_6H_5CH{=}CH{-}CH{=}CHC_6H_5$ ($\lambda_{\text{max.}} = 334$ mμ), and Blout and Fields[8] have reported that polyene azines of the generic formula $CH_3(CH{=}CH)_nCH{=}N{-}N{=}CH(CH{=}CH)_nCH_3$ have maximum absorption bands at shorter wave lengths than do the corresponding aliphatic polyene hydrocarbons with the same number of double bonds.

Lewis and Calvin have explained this on the basis of the "strain" theory by saying that due to the highly strained N=N bond in one of the predominant excited states of benzalazine



the potential energy of the excited state is raised. Although the ground state of the azine may lie above that of the diene, there is a larger difference between the energies of the first excited state and the ground state for the azine to the extent that it absorbs at shorter wave lengths. Blout and Fields have offered a different explanation. Their concept is to place greater emphasis on the contribution of forms Ib and Ic than on Ia to the resonance of the azines which, they believe, favors absorption at shorter wave lengths.[9]

$$CH_3{-}CH{=}CH{-}CH{=}N{-}N{=}CH{-}CH{=}CH{-}CH_3 \quad \text{I}$$

$$CH_3{-}\overset{\mp}{C}H{-}CH{=}CH{-}N{=}N{-}CH{=}CH{-}\overset{\pm}{C}H{-}CH_3 \quad \text{Ia}$$

$$CH_3{-}\overset{+}{C}H{-}CH{=}CH{-}\overset{-}{N}{-}N{=}CH{-}CH{=}CH{-}CH_3 \quad \text{Ib}$$

$$CH_3{-}CH{=}CH{-}CH{=}\overset{-}{N}{-}N{-}CH{=}\overset{+}{C}H{-}CH_3 \quad \text{Ic}$$

When the three compounds, glyoxaldianil ($C_6H_5N{=}CH{-}CH{=}NC_6H_5$), diphenylbutadiene and benzalazine are considered from Lewis' and Calvin's viewpoint, one may expect the dianil to absorb at longer wave lengths than the diene because, first, the dianil possesses two stronger chromophores and, second, the resonance of structures IIa, IIb and IIc for the dianil makes a greater contribution to the excited state than does the resonance of the corresponding ionic forms of the hydrocarbon.

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(1) Data presented before the Organic Division of the American Chemical Society, Sept., 1947.

(2) Present address: Duriron Co., Dayton, Ohio.

(3) G. N. Lewis and M. Calvin, *Chem. Reviews*, **25**, 273 (1939).

(4) S. Dutt, *J. Chem. Soc.*, 1171 (1926).

(5) A. A. Kharkharov, *Chem. Abstracts*, **34**, 4065 (1940).

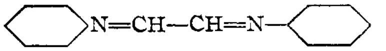
(6) L. N. Ferguson, *Chem. Reviews*, in press.

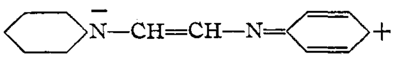
(6a) S. H. Lee and F. A. Matsen, Paper number 33 presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at Portland, Ore., September 14, 1948.

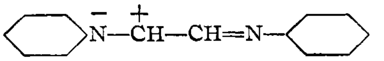
(7) The word "Strain" is used as a mechanical way of referring to the relative potential energy of a particular structure.

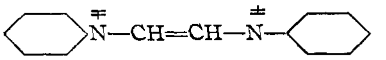
(8) E. R. Blout and M. Fields, THIS JOURNAL **70** 189 (1948).

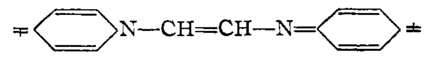
(9) The author is of the opinion that due to the greater electronegativity of nitrogen over carbon, the forms Ib and Ic do make a contribution to the resonance of the azines but this only tends to lower the potential energy of the excited states and would lead to absorption at longer wave lengths than the azines might have if these ionic forms were not possible contributors. This contribution, however, is too small to outweigh the opposite effect caused by the strain in the N=N bond.


II


IIa


IIb


IIc


IId

Hence, one may anticipate the decreasing order of the chromophoric power of these three classes of compounds to be dianil, butadiene, azine. To verify this hypothesis, a number of dianils and azines were prepared and studied spectroscopically. These compounds are listed in Table I, together with their $\lambda_{max.}$ and $\epsilon_{max.}$, and their spectra are drawn in Figs. one to seven.

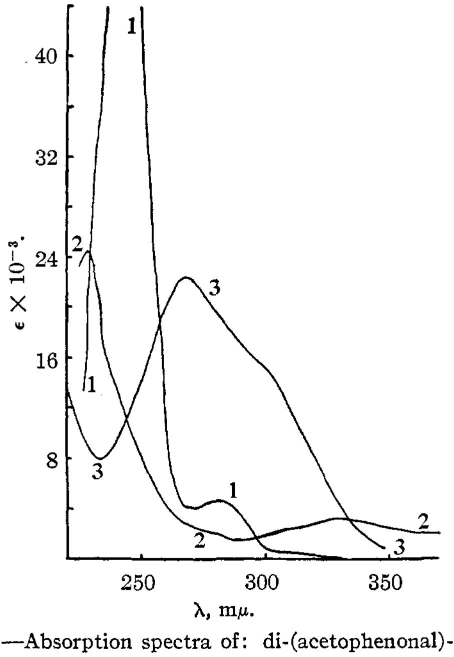


Fig. 1.—Absorption spectra of: di-(acetophenonal)-ethylenediamine, 1; diacetyldianil, 2; acetophenonazine, 3.

From the spectra it can be seen that the decreasing order of the longest wave length of absorption for compounds 10, 10a and 10b is in the order dianil, diene, azine. In addition, the dianils 5a and 6a have maximum absorption bands at longer wave lengths than do the corresponding azines 5 and 6. The hypsochromic shift in going from 8 to 8a cannot be explained satisfactorily. Unfortunately, all attempts to isolate the parent compound glyoxal dianil, $C_6H_5N{=}CH{-}CH{=}NC_6H_5$, were unsuccessful.

Upon looking at compounds 7 with 7a, 2 with 2a and 9 with 9a it is noted that there results a large difference between the maxima of the dianils and the azines when the hydrogen atoms on the methine carbon atoms have been replaced by

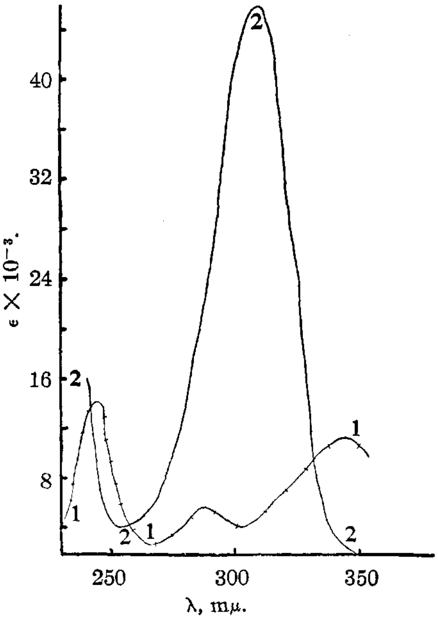


Fig. 2.—Absorption spectra of: glyoxaldi-(*p*-hydroxyanil), 1; *p*-hydroxybenzalazine, 2 (from reference in footnote a to Table I).

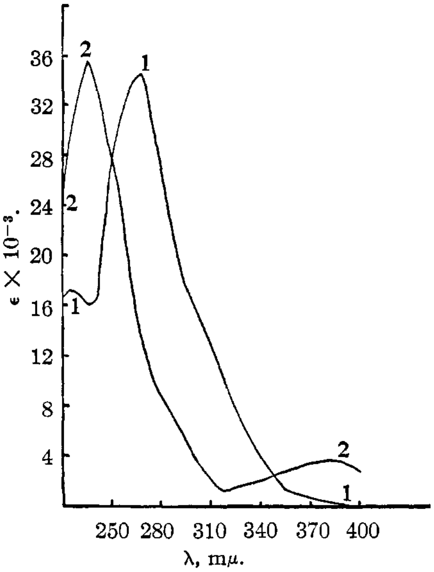


Fig. 3.—Absorption spectra of: *m*-nitroacetophenonazine, 1; diacetyldi-(*m*-nitroanil), 2.

methyl groups. This perhaps is due to three factors: 1, the absence of the highly strained N=N bond in the excited state; 2, a hypsochromic effect in the ketazines due to steric hindrance,[10] and 3,

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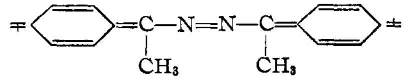
(10) Spacial interference of the methyl groups prevent the coplanarity of the molecule such as is required for the resonant forms



This has been pointed out by Blout, Eager and Gofstein (THIS JOURNAL, **68**, 1983 (1946)) for a number of ketazines and is further observed for the pairs of compounds 6 with 7 and 8 with 9.

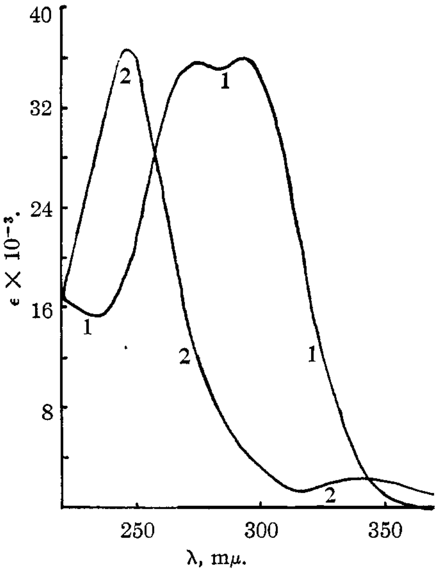


Fig. 4.—Absorption spectra of: *m*-nitrobenzalazine, 1 (from unpublished work by Ferguson and Branch); glyoxaldi-(-*m*-nitroanil), 2.

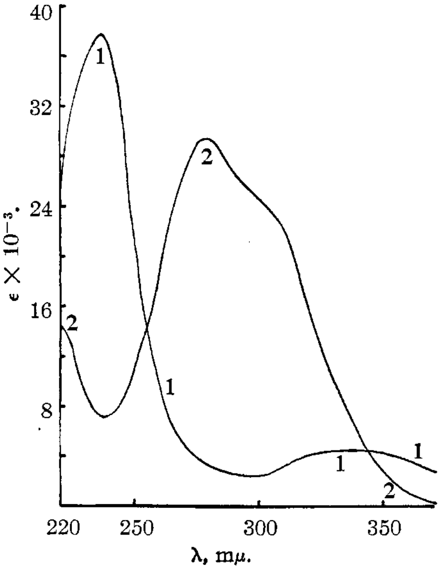


Fig. 5.—Absorption spectra of: diacetyldi-(*p*-bromoanil), 1; *p*-bromoacetophenonazine, 2.

a bathochromic effect by the methyl groups on the N=C—C=N system as observed when comparing the compounds 8a with 9a and 6a with 7a. This is the usual bathochromic effect of alkyl groups on a conjugated double bond which has been attributed to hyperconjugation.[11] This auxochromic effect by methyl groups is also revealed by the pair of compounds 3 and 4 where the steric factor, found in ketazines is absent.

Other points to be noted about the spectra are: 1, the large decrease in $\epsilon_{\max.}$ in going from the C=N—N=C to the N=C—C=N system, 2, the close similarity of the absorption bands for the pairs of compounds 5 with 10 and 5a with 10a indicates the absence of association of the hydroxy compounds through hydrogen bonds, 3, the "insulation" effect, illustrated by comparing compound 1 and 3, is masked when comparing compound 2 with 4 because of the hypsochromic steric effect of the methyl groups in 2.

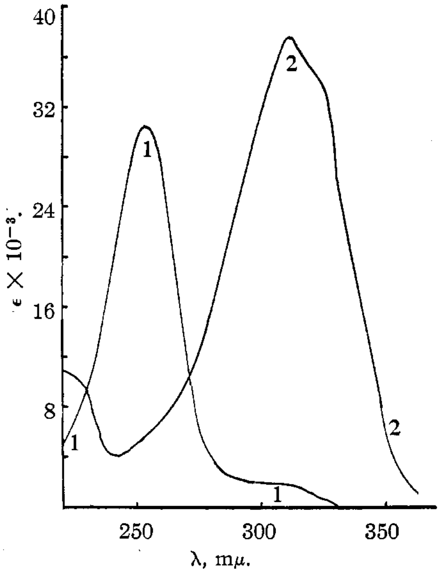


Fig. 6.—Absorption spectra of: glyoxaldi-(*p*-bromoanil), 1; *p*-bromobenzalazine, 2.

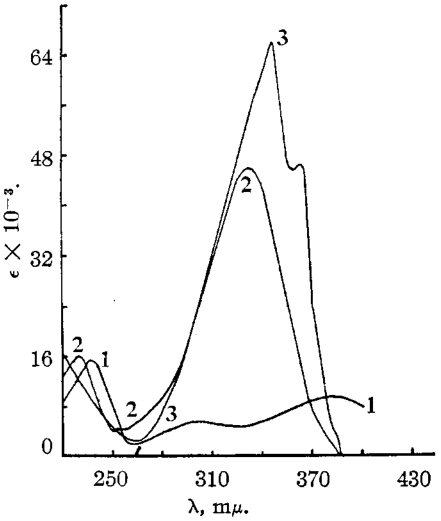


Fig. 7.—Absorption of: 1, glyoxaldi-(*p*-methoxyanil); 2, *p*-methoxybenzalazine; 3, 1,4-di-(*p*-methoxyphenyl)-butadiene-1.

Experimental

The compounds studied were prepared by one of four general procedures, which were: A, Mix the amine and carbonyl compound in 50 to 70% alcohol, warm a short period on the steam-bath and cool over a period of several hours. B, Identical to A except that 2 *N* acetic acid was the solvent. C, Identical to A except that H_2O was the solvent. D, Dissolve glyoxal bisulfite in 2 *N* acetic acid

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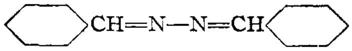
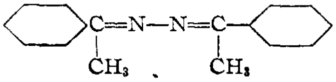
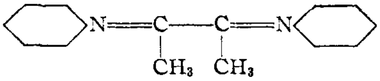
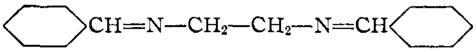
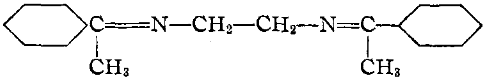
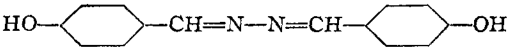
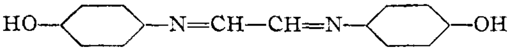
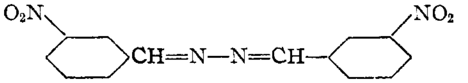
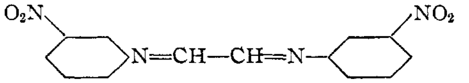
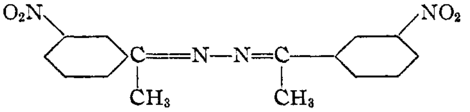
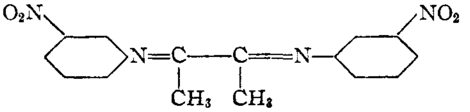
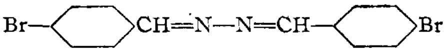
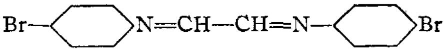
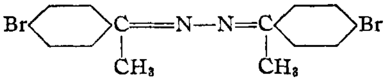
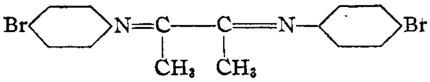
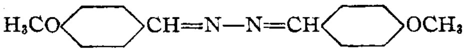
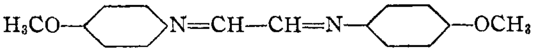
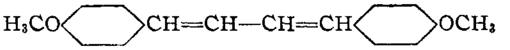
[11] R. S. Mulliken, *J. Chem. Phys.*, **7**, 339 (1939).

TABLE I

WAVE LENGTHS AND MOLECULAR EXTINCTION COEFFICIENTS OF THE MAXIMUM ABSORPTION BANDS OF SOME AZINES AND DIANILS

	Compound	$\lambda_{max.}$, mμ	$\epsilon_{max.}$	$\lambda'_{max.}$, mμ	$\epsilon'_{max.}$	$\lambda''_{max.}$, mμ	$\epsilon''_{max.}$
1		301.1[a]	38,000	213	17,000		
2		267.5	22,500				
2a		331	2,875	228	24,600		
3		247[a]	29,800				
4		280	4,360	243	49,900		
5		333[a]	46,000	228.5	18,000		
5a		388	9,740	301	5,780	236	14,150
6		294[b]	36,200	225	17,000		
6a		333	2,080	245	36,800		
7		266	34,900	225	17,450		
7a		375	3,460	234	35,750		
8		311.5	37,800	221	13,400		
8a		299-302[c]	1,830	254	30,600		
9		279	29,300				
9a		336	4,560	236	37,550		
10		331	45,900	229	16,260		
10a		382	9,470	300	5,810	236	15,410
10b		363	46,600	345	66,000		

[a] Values for these compounds taken from Ferguson and Branch, THIS JOURNAL, 66, 1467 (1944). [b] Value from unpublished work of L. N. Ferguson and G. E. K. Branch. [c] Shoulder.

and the amine in an equal volume of alcohol, mix and heat on the steam-bath for about half an hour and cool over a period of several hours. Ninety-five per cent. ethanol was always the solvent for recrystallization unless otherwise specified.

The absorption measurements were made using a Beckman Photoelectric Quartz Spectrophotometer, Model DU, with 1-cm. square, fused silica absorption cells. Ninety-five per cent. ethanol served as the solvent. The absorption by compounds 2a, 5a, and 10a was found to slowly increase during the measurement of their spectra, this increase being more marked in the regions of maximum absorption.

Acetophenonazine, $[C_6H_5(CH_3)C{=}N{-}]_2$.—By procedure A or B: m.p. obs. 120–121°; lit. 121° (Blout, Eager and Gofstein, ref. 10).

p-Bromoacetophenonazine, $[p\text{-}BrC_6H_4(CH_3)C{=}N{-}]_2$.—By procedure A: m.p. obs. 159–160°. *Anal.* Calcd. for $C_{16}H_{14}N_2Br_2$: C, 48.8; H, 3.55. Found: C, 48.9; H, 3.76.

m-Nitro-acetophenonazine, $[m\text{-}O_2N{-}C_6H_4(CH_3)C{=}N]_2$.—By procedure A: m.p. obs. 197–198°; lit. 194–195°. Knöpfer, *Monatsh.* **30**, 36 (1909).

Diacetyldianil, $[C_6H_5N{=}(CH_3)C{-}]_2$.—By procedures A or B; Procedure C not successful: m.p. obs. 136–137°;

lit. 139–140°; H. von Pechmann, *Ber.*, **21**, 1415 (1888); Lehr and Bloch, *Helv. Chim. Acta*, **28**, 1413 (1945).

Diacetyldi-(*m*-nitroanil), $[m\text{-}O_2NC_6H_4N{=}(CH_3)C{-}]_2$.—By procedure B: Procedure A not successful: m.p. obs. 112–113°. *Anal.* Calcd. for $C_{16}H_{14}O_4N_4$: N, 17.2. Found: N, 17.2.

Diacetyldi-(*p*-bromanil), $[p\text{-}BrC_6H_4N{=}(CH_3)C{-}]_2$.—By procedure A: m.p. 181.5–182.5°; lit. 182–183°, Lehr and Bloch, *Helv. Chim. Acta*, **28**, 1413 (1945).

Glyoxaldianil, $[C_6H_5N{=}CH{-}]_2$.—Procedure A gave resins from which crystalline products could not be obtained. Procedures B, C, and D gave non-recrystallizable amorphous powders with m.p.'s 80–81°, 105–110° and 125–126°, respectively. Its synthesis was abandoned.

Glyoxaldi-(*p*-bromanil), $[p\text{-}BrC_6H_4N{=}CH{-}]_2$.—By procedures A or D: m.p. obs. 181–181.5°; *Anal.* Calcd. for $C_{14}H_{12}N_2Br_2$: C, 45.7; H, 3.26. Found: C, 44.3; H, 2.97.

Glyoxaldi-(*p*-methoxyanil), $[p\text{-}CH_3OC_6H_4N{=}CH{-}]_2$.—By procedures A and B: m.p. obs. 155°; lit. 158°, Lehr and Bloch, *Helv. Chim. Acta*, **28**, 1413 (1945).

Glyoxaldi-(*p*-hydroxyanil), $[p\text{-}HOC_6H_4N{=}CH{-}]_2$.—By procedure A: m.p. obs. 190–191°. *Anal.* Calcd. for $C_{14}H_{12}O_2N_2$: C, 70.0; H, 5.0. Found: C, 70.2; H, 6.0.

Glyoxaldi-(*m*-nitroanil), $[m\text{-}O_2NC_6H_4N{=}CH]_2$.—By procedure D: m.p. obs. 202–203°. *Anal.* Calcd. for $C_{14}H_{10}N_4O_4$: C, 56.4; H, 3.46. Found: C, 55.86; H, 3.74.

1,4-Di-(*p*-methoxyphenyl-butadiene-1,3, $[p\text{-}CH_3OC_6H_4{-}CH{=}CH{-}]_2$.—Prepared according to some unpublished work by Fieser and Potter. Mixed one half mole of freshly distilled anisaldehyde, one-fourth mole of succinic acid, and one-half mole of litharge in 150 cc. of acetic anhydride, and heated on a hot-plate under a reflux condenser for five hours. Then was added 200 cc. of 80% HOAc, the soln. cooled overnight, and the crystals filtered and recrystallized from *n*-propanol; colorless crystals, m.p. 222.5–223.5°.

4,4-Dibromobenzaldazin, $[p\text{-}BrC_6H_4CH{=}N{-}]_2$.—By procedure A: m.p. obs. 223.5°–224.5°, lit. 221; L. Gattermann, *Ann.*, **393**, 223(1912).

4,4-Dimethoxybenzaldazin, $[p\text{-}CH_3OC_6H_4CH{=}N{-}]_2$.—By procedure A: m.p. obs. 167–168°; lit. 168°; G. Knöpfer, *loc. cit.*

Di(acetophenonal)-ethylenediamine, $[C_6H_5(CH_3)C{=}N\text{-}CH_2{-}]_2$.—By procedure A: (drop HOAc added); white crystals from ligroin, m.p. 110–111°; *Anal.* Calcd. for $C_{18}H_{20}N_2$: N, 10.6. Found: N, 10.3.

Acknowledgment.—The authors are indebted to Mr. Theodore Austin, instructor of chemistry in Howard University, for drawing the spectra.

Summary

The order of chromophoric power for the systems dianil, diene, and azine is discussed and illustrated to be decreasing in the order named. A bathochromic effect by substituting methyl groups upon the methine carbon atoms of the dianil system is noted.

HOWARD UNIVERSITY
WASHINGTON 1, D. C.

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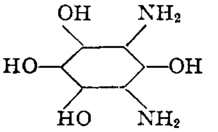
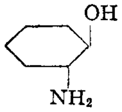
Stereochemistry of Cyclic Amino-alcohols. Inversion, Retention and Participation[1]

BY G. E. MCCASLAND,[2] R. K. CLARK, JR.,[3] AND HERBERT E. CARTER

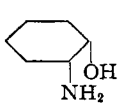
The isolation of streptamine (I),[4] one of the three major degradation products of streptomycin, has stimulated interest in the stereochemistry of polysubstituted alicyclic compounds, and of cyclic aminoalcohols in particular. Streptamine is one of the twenty possible diastereoisomeric forms of 1,3-diamino-2,4,5,6-tetrahydroxycyclohexane. Of these forms, eight are *meso* and twelve racemic, and the recent synthesis[5] of streptamine from glucosamine indicates that "natural" streptamine is the all-*trans*, *meso* form. In support of stereochemical studies on streptamine, model compounds of simpler structure were investigated. For this purpose the 2-aminocyclohexanols were selected.



I



II



III

Both the *cis* and *trans* forms of 2-aminocyclohexanol lack a plane of symmetry and hence are theoretically resolvable. Thus the configurations cannot be established by resolution of the *trans* isomer, as with the diol or diamine. Experimentally, two racemic forms of 2-aminocyclohexanol are known. The first, isomer "A," melts at 68°; the second, isomer "B," melts at 72°. The melting points of a number of derivatives of "A" and "B" are given in Table I.

Isomer "A" was first prepared in 1905 by Brunel[6a] by the amination of cyclohexene oxide, and also can be obtained by the amination of cyclohexene halohydrin,[6b] or by the reduction of 2-hydroxycyclohexanone oxime.[6c] The preparation of the "B" isomer was first described in a 1936 patent,[7] and few details regarding it have been published. An alternate preparation of the "B" isomer (N-benzoyl), by the tosylation and detosylation of the "A" N-benzoyl derivative, is described below.

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[2] Present address: Chemistry Department, University of Toronto.

[3] Present address: Abbott Laboratories, North Chicago.

[4] H. E. Carter, *et al.*, *Science*, **103**, 53 (1946).

[5] Wolfrom and Olin, Abstracts, Chicago Meeting, A.C.S., April, 1948, p. 5Q.

[6] (a) Brunel, *Ann. chim.*, [8] **6**, 253 (1905); (b) Osterberg and Kendall, THIS JOURNAL, **42**, 2616 (1920); (c) Wilson and Read, *J. Chem. Soc.*, 1269 (1935).

[7] *Chem. Abs.*, **32**, 7055 (1938); *Chem. Zentr.*, **108**, I, 2260 (1937).