

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

Polarographic Study of the Restriction of the Tautomerism of Amidines by Hydrogen Bonding¹

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The association of certain amidines through hydrogen bonds² led Hunter³ to the conclusion that in the case of an unsymmetrically substituted amidine the dual character shown in reaction is in fact due to a "homogeneous" substance in which "separate tautomers . . . do not exist." It does not impair the validity of Hunter's conclusion that, since association of amidines is not extensive, the two tautomers must be momentarily present in quantity. Acids or bases rupture the associative bonds, but the resulting cation or anion then consists of a resonance hybrid in which the identity of each tautomer is wholly lost. It is conceivable that association may occasionally attain to the state of bimolecular salt formation.⁴ These considerations appear to justify the inference that unsymmetrical amidines, whether submitted to neutral, acid or alkaline conditions, exist in forms which are not distinguishable.

Attempts to fix a single tautomer or both tautomers or to estimate the proportion of each tautomer by alkylation failed to yield decisive results, as two products were obtained,⁵ the reactions involved being too slow to reveal the momentary state of the tautomeric system; the results of partial hydrolysis are without significance for the same reason. Claims of the isolation of one or both tautomers should be accepted with caution. The alleged preparation of two tautomeric 2-phenylnaphthimidazoles by Galimberti⁶ has recently been disposed of by Kelly and Day⁷ and by Hunter.³ There remain unaccounted for only the two isomeric (and interconvertible) diphenylimidazoles, the existence of which was confirmed by Burtles and Pyman⁸ (and which Weidenhagen and Hermann⁹ considered to be polymorphs), and the arylsulfonamidines ($\text{ArSO}_2\text{NHCR}=\text{NH}$) reported as separable tautomers by Barber.¹⁰

Hunter's generalized conclusions³ with respect to the results of intermolecular hydrogen bonding in mesohydric systems are so stated as to exclude the possibility that in any case a single tautomer has a real existence. Without questioning the general validity of these conclusions, or their value in clarifying a situation hitherto some-

times misapprehended, it may be suggested that an intramolecular immobilizing influence able to affect the normal mobility of the amidine hydrogen atom or the double bond of an unsymmetrical amidine may lead to stabilization of one of the tautomers to whatever extent this influence is able to prevail over the tendency to intermolecular hydrogen bonding or to prototropy. The influences which might depress the mobility of either the double bond or the amidine hydrogen, and which at the extreme might stabilize one tautomeric structure, include the following. (1) A strongly polar group located unsymmetrically with respect to the two nitrogen atoms and conceivably able to stabilize one tautomer. (2) A structure such as to interfere sterically with prototropy or with associative hydrogen bonding.¹¹ (3) A structural condition which renders the amidine hydrogen inactive, *i. e.*, disinclined to migrate or to engage in hydrogen bonding, as for example a tautomeric form in which it is attached to carbon rather than nitrogen.¹² (4) A structure such that one tautomer is stabilized by conjugation, the amidine double bond in one tautomer but not in the other being part of an extended conjugate system.¹³ (5) A group or atom so placed and of such character as to permit establishment of an intramolecular hydrogen bond (chelate ring) involving the amidine hydrogen when it is attached to a certain one of the nitrogen atoms, thus depriving it more or less completely of freedom either to migrate or to engage in intermolecular hydrogen bonding. Hunter and Marriott² assumed chelation to explain the observed low degree of association of 2-*o*-nitrophenyl-4,5-diphenylbenzimidazole and 2-benzoylbenzimidazole and the absence of association of the phenylhydrazone of the latter, but in each case the assumed chelation is without significance with respect to the tautomeric system since it can involve the amidine hydrogen whether attached to one nitrogen or the other. That intermolecular hydrogen bonding can be decreased or

(11) The comparative immunity of hydrogen atoms to steric blocking, as shown for example by the results of Cornubert, *et al.*, *Bull. soc. chim.*, **43**, 807 (1928), (5), **2**, 195 (1935), with hindered ketones, suggests the probable ineffectiveness of such an influence. The findings of Fuson and co-workers, *THIS JOURNAL*, **62**, 3250 (1940); **63**, 2639, 2643 (1941); **64**, 2886, 2888 (1942), with 1,2-dimesityl-1-propen-1-ol make it appear wise to consider the possibility open.

(12) This condition is possible only in imidazoles such as the diphenylimidazoles mentioned^{8,9} and not in condensed imidazole systems or in amidines.

(13) This viewpoint is recognizable in some of Pyman's speculations on directed alkylations,^{8b} and the same principle may be involved in the stability of Fuson's enol¹¹; its possible usefulness as applied to amidines and to the two diphenylimidazoles mentioned is to be tested in experiments now in progress.

(1) Presented before the Philadelphia Section of the American Chemical Society, June, 1945.

(2) Hunter and Marriott, *J. Chem. Soc.*, 777 (1941).

(3) Hunter, *ibid.*, 806 (1945).

(4) Shriner and Neumann, *Chem. Rev.*, **35**, 379 (1944).

(5) (a) Pyman, *J. Chem. Soc.*, 367, 3359 (1923); (b) Chew and Pyman, *ibid.*, 2318 (1927).

(6) Galimberti, *Gazz. chim. ital.*, **63**, 96 (1933).

(7) Kelly and Day, *THIS JOURNAL*, **67**, 1074 (1945).

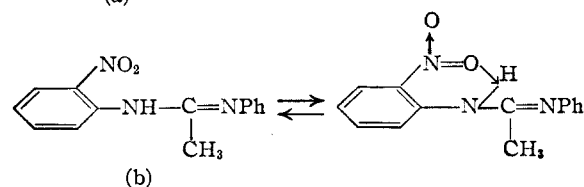
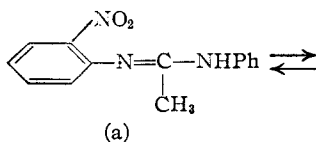
(8) Burtles and Pyman, *J. Chem. Soc.*, **123**, 361 (1923).

(9) Weidenhagen and Hermann, *Ber.*, **68**, 1957 (1935), footnote.

(10) Barber, *J. Chem. Soc.*, 101 (1943).

excluded by internal hydrogen bonding has been demonstrated, for example by study of the association of the isomeric nitrophenols.¹⁴ Experiments to test the extension of this method to amidines are described below.

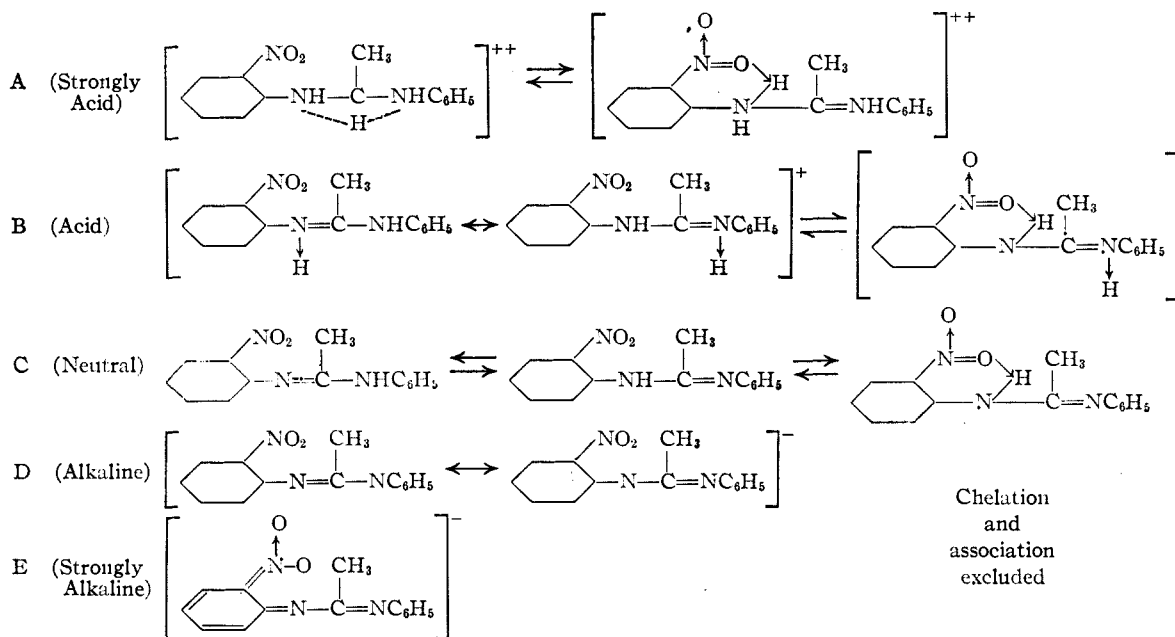
The compounds selected for experimental testing of the possibility that internal hydrogen bonding may restrict prototropy or association of amidines are N-phenyl-N'-o-nitrophenylacetamidine (I), N-phenyl-N'-m-nitrophenylacetamidine (II) and N-phenyl-N'-p-nitrophenylacetamidine (III), of which the structure of III admits of chelation.¹⁵



Any resulting differences in I, as compared with II and III, may be recognized by light absorption methods, by X-ray diffraction analysis, by polaro-

graphic study of the relative reducibilities of the nitro groups in the three isomeric amidines, or by molecular weight determinations. The last two methods were used in the initial examination reported in this paper, in which the polarographic data are interpreted in the manner made familiar by Astle¹⁶ in studies of nitrophenols. Involvement of the nitro group and the amidine hydrogen in a chelate ring would interfere with the normal resonance of the former, and might be regarded as an incipient hydrogenation, making the nitro group of I more readily reducible than that of II or III; this was the result obtained, both polarographically and catalytically. It was found further that III is more associated than I under neutral conditions (in naphthalene). It is concluded that the greater reducibility of I, and its lesser association (as compared with III), may be attributed to chelation.

Since the state of the amphoteric amidine system is subject to change depending upon the nature of the environment the polarographic examinations were made at various points in the pH range 2.2 to 14.5.¹⁷ The possible states are indicated for compound I in the accompanying scheme. Similar schemes for II and III would differ only in the omission of the chelate forms and of the quinonoid form in the case of II.



(14) Sidgwick, Taylor and Baker, "The Organic Chemistry of Nitrogen," Oxford University Press, New York, N. Y., 1937, p. 268.

(15) Chelation could occur as shown with either geometrically isomeric form of tautomer b. Tautomer a, in its anti-methyl form, might exist with an 8-atom chelate ring with the amidine hydrogen fixed on the phenyl-nitrogen. The two chelate forms would require equivalent interpretations of the results; the 6-atom chelate ring will be used in this paper.

Forms A and E are not known to be isolable; their existence, and also that of the chelate structures, is inferred from the experimental results.

Discussion of Results.—The polarographic reduction in each case affected only the nitro

(16) Astle and McConnell, *THIS JOURNAL*, **65**, 35 (1943); Astle and Cropper, *ibid.*, **65**, 2395 (1943); Astle and Stephenson, *ibid.*, **65**, 2399 (1943).

(17) In 50% ethanol; the pH values are those of the aqueous buffer before dilution with ethanol.

group and not the amidine structure, as was shown in attempts to reduce *N,N'*-diphenylacetamidine, which developed no diffusion current within the potential range up to sodium ion discharge. In the reductions of the three phenyl nitrophenylacetamidines the first wave in each case was well defined and showed a steady state of equilibrium; representative tracings of the curves for several pH values are shown in Fig. 1. The

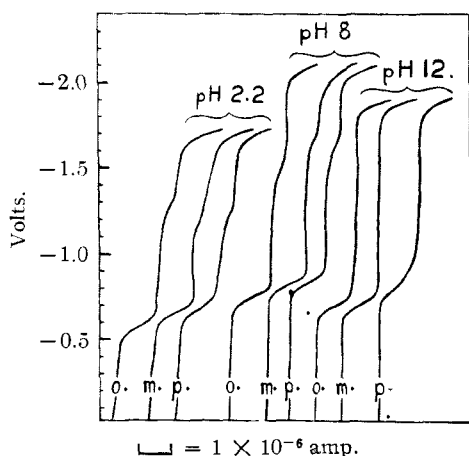


Fig. 1.—Current-voltage curves for $2.5 \times 10^{-4} M$ *N*-phenyl-*N'*-*o*-nitrophenylacetamidine; *N*-phenyl-*N'*-*m*-nitrophenylacetamidine; and *N*-phenyl-*N'*-*p*-nitrophenylacetamidine at 25° ; $m^{2/3}t^{1/6} = 1.14 \text{ mg.}^{2/3} \text{ sec.}^{-1/2}$.

second wave was approximately one-half the height of the first though less sharply defined, and did not in all cases level off before discharge of the sodium ion of the supporting electrolyte. Above pH 8 the second wave disappeared. The diffusion current at each pH is given in Table I. As

TABLE I

THE EFFECT OF pH ON THE DIFFUSION CURRENT FOR THE *N*-NITROPHENYL-*N'*-PHENYLACETAMIDINES

$m^{2/3}t^{1/6} = 1.14 \text{ mg.}^{2/3} \text{ sec.}^{-1/2}$ Concentration of solutions 2.5×10^{-4} molar. Diffusion current in microamperes.

pH	<i>ortho.</i>		<i>para.</i>		<i>meta.</i>	
	First wave	Total wave	First wave	Total wave	First wave	Total wave
2.2	1.15	1.78 ^a	1.26	1.70 ^a	1.15	1.68 ^a
3.0	1.13	1.73 ^a	1.24	1.68 ^a	1.13	1.65 ^a
4.0	1.12	1.68 ^a	1.28	1.70 ^a	1.07	1.64 ^a
5.0	1.16	1.62 ^a	1.23	1.63 ^a	1.10	1.66 ^a
6.0	1.39	1.91	1.21	1.72 ^a	1.10	1.64 ^a
7.0	1.34	1.63	1.08	1.78	1.11	1.63
8.0	1.21	1.61	1.09	1.48	1.15	1.48
9.4	1.07		1.06		1.08	
10.9	1.12		1.17		1.16	
12.1	1.13		1.21		1.13	
14.5	0.78		0.76		0.76	

^a Na ion discharge interferes.

explained below, it appears that the first wave represents reduction to the hydroxylamino stage (at pH 14.5 in part only to the nitroso stage), and the second wave reduction to the amino stage.

The current-voltage curves for the three amidines indicate the extent of reduction of each to be the same for each pH value (Fig. 1).

TABLE II

THE EFFECT OF pH ON THE REDUCTION POTENTIALS OF THE *N*-NITROPHENYL-*N'*-PHENYLACETAMIDINES

Half-wave potential (S.C.E.) in volts

pH	<i>ortho.</i>		<i>para.</i>		<i>meta.</i>	
	First wave	Second wave	First wave	Second wave	First wave	Second wave
2.2	-0.50	-1.14	-0.60	-1.13	-0.58	-1.18
3.0	-.52	-1.28	-.60	-1.19	-.58	-1.26
4.0	-.54	-1.30	-.65	-1.28	-.59	-1.36
5.0	-.58	-1.34	-.67	-1.43	-.61	-1.41
6.0	-.59	-1.34	-.68	-1.46	-.63	-1.45
7.0	-.61	-1.36	-.70	-1.48	-.67	-1.51
8.0	-.67	-1.38	-.75	-1.52	-.74	-1.58
9.4	-.67		-.76		-.74	
10.9	-.72		-.83		-.75	
12.1	-.76		-.90		-.78	
14.5	-.77		-.87		-.76	

The half-wave reduction potential (Fig. 2 and Table II) of the *o*-nitro compound I is consistently about 0.1 volt more positive than that of the *p*-isomer III, with that of the *m*-nitro isomer II intermediate, throughout the range pH 2.2 to 13. The plateaus which appear at successively more negative potentials, associated with successively higher pH values (*viz.*, pH 2.2-3, 5-6, 8-9.4 and 12-14.5), may be interpreted by reference to the scheme of relationships shown above. It is inferred that at the highest acidity (pH 2.2 to 3) the dipositive ion A is present, and that the other pH values specified represent, respectively, the conditions under which there exist the cation B, the neutral amidine C and the anion D. If this interpretation is correct it may be surmised, since the curve for II lacks the second plateau, that the monospecific and dipositive ionic forms of II do not differ greatly in acid strength, so that there is no point in the acid range where II is present almost wholly in a single ionic form. A further change in the anions of I and III to the quinonoid-nitronic anions is possible at high alkalinity. This is not uniformly apparent in the polarographic findings, but is suggested by the behav-

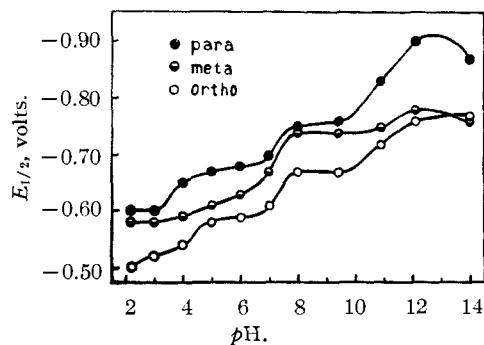


Fig. 2.—Change of half-wave potential (first wave) with pH.

iors of the three compounds with sodium ethoxide in anhydrous ethanol, I and III giving strongly colored solutions, while II showed no increase in the usual pale yellow color of the amidine in alcohol.

From Fig. 2 it can be seen that the *o*-nitro compound I is more readily reduced than the isomers II and III except in strongly alkaline solution. At *pH* 2.2 and at *pH* 7 to 9.4 the half-wave potentials of II and III differ by amounts not more than about twice the precision of the measurements, while the values for I are much less negative. The comparatively greater reducibility of the *o*-nitro compound is attributed to hydrogen bonding, as represented in the scheme above.¹⁸ The possibility that the differences between the reducibility of I and the reducibilities of II and III may be diminished because of association of II and III through the N-H-O linkage appears to be excluded by simultaneous consideration of the reduction results and the association results as obtained for I and III. Molecular weight determinations by the freezing point method, using naphthalene as solvent, showed that neither I nor III is extensively associated, but that the association factor M/M_0 for III is greater than that for I; the values found at 0.12 molal concentration were 1.02 for I and 1.12 for III, the difference of 10% being estimated as about five times the error of the measurements. There is no definite evidence to show that the indicated associations involve N-H-O linkages between amidine molecules,¹⁹ which would be expected to increase the reducibility of the nitro group of III, rather than N-H-N linkages, which would have no such effect, but it seems significant that the reducibility

(18) The observation by Shikata and Taguchi, *Mem. Coll. Agr. Kyoto Imp. Univ.*, **29**, 1 (1934), that *m*-nitroaniline was reduced at lower potential than the *p*- and *o*-isomers, of which the latter appears to be capable of chelation, is inconsistent both with the results of Astle and McConnell¹⁶ for the isomeric nitrophenols and with our results for the phenylnitrophenyl acetamidines. Attention may be called to the use, by Shikata and Taguchi, of the tangent method for obtaining the reduction potentials, this being regarded at present as an inferior procedure (Kolthoff and Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 147), and to the noticeably poor agreement of the earlier results of Shikata and Watanabe, *J. Agr. Chem. Soc. Japan*, **4**, 924 (1928), on the nitrophenols with the results of Astle and McConnell. The similarity of the nitroanilines and the phenylnitrophenylacetamidines is superficial, for they are related as are the nitroanilines and the nitroacetanilides, the acetamide side chain attached to the nitrophenyl group being the nitrogen-system equivalent of the acetamino group. No polarographic data for the nitroacetanilides are available, but it may be deduced that the influence of this polyfunctional side chain would be less simple than that of the unsubstituted amino group.

(19) In the reduction experiments association of amidine and solvent alcohol through N-H-O or O-H-O linkages is to be assumed, and this may be competitive with association of amidine molecules with one another and with chelation in I. Solvation would presumably affect most strongly the *o*-isomer, since it is the most soluble, and would operate, if at all, to decrease the differences between the *o*-isomer and the *m*- and *p*-isomers. The observed differences in reducibility in alcohol, whether obtained polarographically or catalytically, are judged to be the more significant because they surmount the equalizing influences mentioned. By using naphthalene as solvent the results for association of the amidines may be interpreted without complications due to solvation; the only obvious explanation of the lesser association of I is that it is chelated.

of I was found to be markedly greater than that of III in the region *pH* 7 to 9.4, *i. e.*, near neutrality, under which conditions III is associated nearly 10% more than I. These facts are consistent with the conclusions that association of III is largely or wholly through the N-H-N linkage, and that the lesser association of I is the result of chelation. The greater ease of reduction of I as compared with II and III was shown also by the results of catalytic hydrogenations in methanol, using Raney nickel catalyst, the periods required for complete reduction of the nitro group²⁰ being in the ratio I:II:III = 1:4:6. The greater reducibility of I at *pH* 2.2 may indicate that at this relatively high acidity there is some stabilization of the chelate ring.

The relationships just discussed are markedly altered in the *pH* range 12 to 14.5. At this alkalinity the solution of III was deep orange-red in color, suggesting quinonization, while the solutions of I and II showed only the normal yellow color. The increased half-wave potentials for the three isomers above *pH* 10 may be related to the fact that the anion D is incapable of association and exposes to reduction the normal nitro group.

The extent of reduction of the nitro group may be calculated by the Ilkovic equation providing the diffusion coefficient is known. The diffusion coefficient of the amidines was calculated from the Stokes-Einstein equation²¹; the value found, 2.09×10^{-6} cm.²sec.⁻¹, is at best approximate since the amidine molecule probably lacks the spherical form for which the equation is valid. Substitution in the Ilkovic equation gives 4.6 as the number of electrons involved in the first stage of equilibrium (first wave), indicating apparently a four-electron reduction, *i. e.*, to the hydroxylamino stage. In the range *pH* 2.2 to 8, in which two waves were observed, the first wave is about two-thirds of the total wave. If it is assumed that the total wave represents reduction to the amino stage, *i. e.*, a six-electron reduction, it follows that the first wave corresponds to a four-electron reduction, thus confirming the calculated value. At *pH* 14.5, however, the wave was about two-thirds as great as at the lower values, indicating reduction in part only to the nitroso stage.

Experimental

The amidines, prepared from suitable amines and acetylaminates by the method of Hill and Cox,²² were crystallized to constant melting points: N-phenyl-N'-*o*-nitrophenylacetamide (ligroin, then cyclohexane), m. p. 108.0°; N-phenyl-N'-*m*-nitrophenylacetamide and N-phenyl-N'-*p*-nitrophenylacetamide (95% ethanol, then ethanol-water), m. p. 118.3° and 196.4°, respectively; N,N'-diphenylacetamide (ethanol), m. p. 132° (all values corrected).

For the range *pH* 2.2 to 8.0 McIlvaine standard buffer solutions were used, and Sørensen sodium borate-

(20) Under similar conditions N,N'-diphenylacetamide absorbed no hydrogen.

(21) Kolthoff and Lingane, "Polarography," Interscience Publishers, Inc., New York, 1941, p. 49.

(22) Hill and Cox, *THIS JOURNAL*, **48**, 3214 (1926).

sodium hydroxide buffers for pH 9.4 to 12.1; to obtain pH 14.5 the calculated quantity of sodium hydroxide was added. The amidines were dissolved in 95% ethanol to make 5×10^{-4} molar solutions. For each experiment the amidine solution was diluted with an equal volume of the appropriate buffer in the electrolysis cell and was allowed to attain thermal equilibrium in a constant temperature bath held at $25 \pm 0.2^\circ$. The concentrations of amidine (2.5×10^{-4} molar) and of buffer proved to be satisfactory. The use of less alcohol led to separation of solid amidine, and the use of more concentrated buffer solutions led to separation of buffering salts. The buffer action was adequate to yield consistent results which apparently were unaffected by either dissolved carbon dioxide or the negligible quantities of reduction products formed at the cathode.

The measurements were made with a Leeds and Northrup Electro-Chemograph operating at the 10 microampere range of the recorder. The "half-curve" potentials were obtained by manual operation of the polarizer at the end of each run. For each experiment the potential at the anode (quiet mercury pool) was measured against a saturated calomel electrode using a Leeds and Northrup portable potentiometer, and these voltages were used to change all "half-curve" potentials to half-wave potentials referred to the saturated calomel electrode at 25° , as shown in Table II.²³ The dropping mercury cathode operated at a pressure of 35 cm.; the drop time, for open circuit, was about 5.4 seconds. The calibration of the capillary gave $m^2/st^{1/2} = 1.14 \text{ mg.}^{1/2}\text{sec.}^{-1/2}$. Characterization of the capillary according to Müller²⁴ gave a capillary constant $K = 40.94 \text{ cm. sec./mg.}$, and the radius of the capillary orifice $\rho = 18.0 \mu$.

To remove dissolved oxygen from the solution in the electrolysis cell nitrogen was bubbled through it; the nitrogen (from a commercial cylinder) was first passed through distilled water and then through a solution of the same composition as that in the cell. Blanks were run at each pH on the buffer-alcohol solution without amidine, and the readings were used as residual current corrections in obtaining the values of the diffusion currents listed in Table I.

For the cryoscopic determinations of molecular weights in naphthalene the procedure of v. Auwers²⁵ was used. The naphthalene was recrystallized twice from aqueous ethanol. The solute was compressed into pellets. Super-

cooling was held to $0.02\text{--}0.03^\circ$. For each solution at least two separate sets of measurements were made, the individual depressions of the freezing point varying not more than 0.002° . The approximate form of the freezing-point equation was employed in calculating the molecular weights.

Catalytic Reduction.—In each case 4.5 g. (0.0176 mole) of I, II or III was dissolved in 150 ml. of methanol (in which I is most, and III least, soluble), and the solution was transferred to the pressure bottle of an Adams and Vorhees machine.²⁶ About 4 g. of Raney nickel (wet with ethanol) was added, and hydrogenation was effected at an initial pressure of 33–35 lb. per sq. in., the pressures being recorded at five-minute intervals. The times required for complete reduction of the nitro groups of I, II and III were respectively fifteen, sixty and ninety minutes. Hydrogenation was limited to the nitro groups; earlier attempts to hydrogenate the C=N bond of N,N'-diphenylacetamide were unsuccessful.²⁷

Summary

1. The tautomerism of amidines with mobile hydrogen is discussed in the light of recent developments, and with respect to the possibility that influences might be brought to bear to stabilize a single tautomer.

2. Polarographic examination of the three isomeric N-phenyl-N'-nitrophenyl acetamidines indicated the nitro group of the ortho isomer to be much more readily reduced (especially at pH 2.2 and at 7–9.4) than the nitro group of the *m*- or *p*-isomer. Catalytic hydrogenations of the three compounds confirmed this finding. Molecular weight determinations showed the para isomer to be more extensively associated than the ortho isomer. These differences may be explained as the result of internal hydrogen bonding (chelation), a phenomenon possible only in the ortho isomer, and which represents in some degree a stabilization of one tautomer.

(26) "Organic Syntheses," Coll. Vol. I, 1941, p. 66.

(27) The catalytic hydrogenations were run by H. Leon Bradlow.

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(23) The reliability of the method of obtaining half-wave potentials is shown by the value found for cadmium ion in 0.1 *N* potassium chloride solution, *viz.*, $E^{1/2} = -0.60 \text{ v. at } 25^\circ$.

(24) Müller, THIS JOURNAL, **66**, 1019 (1944).

(25) v. Auwers, *Z. physik. Chem.*, **18**, 595 (1895).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

Infrared Absorption Spectra of Tetramethyl Compounds

By C. W. YOUNG,¹ J. S. KOEHLER AND D. S. MCKINNEY

The molecular vibrational spectra of the tetramethyl compounds of C, Si, Sn and Pb, and of the analogous tetramethylammonium ion, have been considered in a number of papers,^{2–12} but as yet no

(1) Present address: Massachusetts Institute of Technology, Cambridge, Mass. This paper is from a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Science in Chemistry, C. I. T., 1946. Presented in part at the April, 1946, meeting of the American Chemical Society in Atlantic City.

(2) K. W. F. Kohlrausch and D. Barnés, *Anales soc. españ. fis. quím.*, **30**, 733 (1932).

(3) K. W. F. Kohlrausch and F. Köppl, *Z. physik. Chem.*, **B26**, 209 (1934).

(4) D. H. Rank and E. R. Bordner, *J. Chem. physik.*, **3**, 248 (1935).

(5) D. H. Rank, *ibid.*, **1**, 572 (1933).

complete assignment of the fundamental frequencies has been given. This paper presents the infrared absorption spectra from 1 to 15μ of tetramethylsilicon and tetramethylgermanium obtained by means of a rock salt prism spectrometer. With the aid of a grating spectrometer, the na-

(6) N. G. Pai, *Proc. Roy. Soc. (London)*, **149**, 29 (1935).

(7) A. B. Duncan and J. W. Murray, *J. Chem. Phys.*, **2**, 146, 642 (1934).

(8) J. T. Edsall, *ibid.*, **5**, 225 (1937).

(9) C. F. Kettering and W. W. Sleator, *Physics*, **4**, 39 (1933).

(10) F. T. Wall and C. R. Eddy, *J. Chem. Phys.*, **6**, 107 (1938).

(11) S. Silver, *ibid.*, **7**, 1113 (1939); **8**, 919 (1940).

(12) T. F. Anderson, *ibid.*, **4**, 161 (1936).