evaporated to dryness under reduced pressure and the residue crystallized as colorless rosettes of needles from ethanol; wt. 0.32 g. (90% yield), m.p. 162–164°; $[\alpha]^{25}D$ +7.8° (EtOH, *c* 0.2), $\lambda_{max,\ min}^{95\%\ EtOH}$ (mμ) 266, 234 (ε 9410, 1470).

Anal. Calcd. for $C_{11}H_{16}N_2O_7S$: C, 41.24; H, 5.04; N, 8.75. Found: C, 41.07; H, 5.01; N, 8.87.

A solution of 1.72 g. (5.34 mmoles) of If and 2.4 g. (16 mmoles) of anhydrous sodium iodide in 50 ml. of dry butanone was refluxed for 2 hr. under an atmosphere of nitrogen. The sodium mesylate was removed by filtration and the filtrate evaporated to dryness under reduced pressure. The pale yellow residue was triturated with cold water, collected, and dried; wt. 1.67 g. (89% yield), m.p. 165–168° dec. (lit.,[2] 168° dec.) alone or when admixed with an authentic sample of 5′-iodo-5′-deoxythymidine.

Methanesulfonyl chloride[8] (0.12 ml., 1.5 mmoles) was added to a solution of 0.4 g. (1.44 mmoles) of Id in 5 ml. of pyridine and the solution held at 0° overnight. Water (1 ml.) was then added, the mixture evaporated to dryness (> 40°) under reduced pressure and a solution of the residue in chloroform was washed successively with 0.1 *N* sulfuric acid, aqueous sodium bicarbonate, and water. The dried (magnesium sulfate) extract was filtered and the filtrate evaporated to dryness under reduced pressure. The residual frothy glass was dissolved in 10 ml. of 95% ethanol, saturated ethanolic ammonia (10 ml.) was added and the solution held at 0° overnight. The solvent was removed under reduced pressure and the residue slowly crystallized at room temperature from ethanol as a colorless solid, wt. 0.21 g., m.p. 156–162°. Recrystallization from ethanol gave small, colorless arrowheads, wt. 0.15 g., m.p. 162–164° alone or when admixed with an authentic sample of Ie. Infrared absorption spectra derived from Ie and this product were essentially superimposable, both exhibiting a strong acetate peak (Nujol) at 5.74 μ.

The original alcohol filtrate was stored in a refrigerator overnight and an additional crop of material was collected; wt. 0.095 g., m.p. 145–150°. The infrared spectrum obtained with this fraction was quite similar to that derived from If with the exception that the former manifested a prominent shoulder at 5.74 μ.

3′-O-Mesylthymidine (Ih).—A solution of 3.4 g. (6.05 mmoles) of Ig[2] in 40 ml. of 80% acetic acid was refluxed for 6 min. and the clear solution evaporated to dryness under reduced pressure. The residue was twice evaporated from ethanol and then triturated with (3 × 25 ml.) boiling ether. The ether-insoluble material crystallized from ethanol as a colorless solid; wt. 1.01 g. (52% yield), m.p. 150–153° dec. A second recrystallization (Norit) from ethanol gave a colorless granular solid, m.p. 152–153° dec.; $[\alpha]^{25}D$ +9.4° (EtOH, *c* 1.15), $\lambda_{max,\ min}^{95\%\ EtOH}$ (mμ) 265, 233 (ε 9867, 2200).

Anal. Calcd. for $C_{11}H_{16}N_2O_7S$: C, 41.24; H, 5.04; N, 8.75. Found: C, 41.23; H, 5 14; N, 8.76.

To a cold solution of 0.16 g. (0.5 mmole) of Ih in 2 ml. of dry pyridine was added 0.1 ml. (1.3 mmoles) of methanesulfonyl chloride and the solution held at 0° overnight. To the clear solution was added *ca.* 0.1 ml. of water and the mixture held at 0° for an additional 0.5 hr. The clear solution was slowly poured into 50 ml. of ice water with vigorous stirring, the solid collected, washed with liberal quantities of water, and dried. A single crystallization from 95% ethanol gave rosettes of colorless needles; wt. 0.145 g. (73% yield), m.p. 166–169° dec., (lit.,[2] 168–169° dec.), $[\alpha]^{25}D$ +8.1° (acetone, *c* 1), $\lambda_{max,\ min}^{95\%\ EtOH}$ (mμ) 263, 233 (ε 8666, 1443).

An authentic sample of Ii prepared from thymidine[2] exhibited the following properties: m.p. 166–169° dec.; $[\alpha]^{23}D$ +7.9° (acetone, *c* 1), $\lambda_{max,\ min}^{95\%\ EtOH}$ (mμ) 263, 233 (ε 8670, 1140).

(8) This procedure essentially duplicates that described in ref. 4.

Synthesis of Imidazo[5, 1-*a*]isoquinoline and -β-carboline Derivatives

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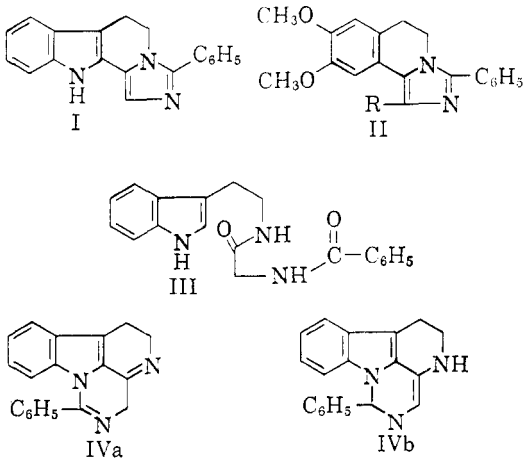
3-Phenyl-5,6-dihydroimidazo[5,1-*a*]-β-carboline (I), which represents a member of a new ring system, was prepared by a series of reactions that are analogous to the synthesis of 3-phenyl-5,6-dihydro-8,9 - dimethoxyimidazo[5,1 -*a*]isoquinoline (II).[1] The preparation of the imidazo-β-carboline derivative was undertaken to test the feasibility of extending to the indole series this double ring closure illustrated by the synthesis of II (R = H)[2] and to submit I for biological testing since II has been found to have amoebicidal properties.[1,3]



Tryptamine was condensed with ethyl hippurate to give (3-indolyl)hippuramide (III) as shown by analysis, absorption spectra and a positive Ehrlich test, which indicates that the indole ring was unsubstituted at the 2-position. The amide was dehydrated with phosphoryl chloride in toluene to afford a basic compound, $C_{19}H_{15}N_3$. The formulation of the base as I is supported by the method of synthesis, by analysis and molecular weight determination, by its chemical properties, and by absorption spectra. In contrast to the starting amide the base gives a negative Ehrlich test and forms a monohydrochloride ($C_{19}H_{16}N_3Cl$) and a monomethiodide ($C_{20}H_{18}N_3I$). The potentiometric titration of the base (I) confirms that it is a monoacidic

(1) R. Child and F. Pyman, *J. Chem. Soc.*, 36 (1931); Ring index no. 2772, A. M. Patterson, L. T. Capell, and D. F. Walker, "The Ring Index," 2nd ed., American Chemical Society, Washington, D. C., 1960.

(2) In the unactivated case, the formation of an imidazo[5,1-*a*]isoquinoline from β-phenylethylhippuramide is not successful; unpublished observations.

(3) T. Kametani, H. Iida, and H. Iwakata, *J. Pharm. Soc. Japan*, **71**, 325 (1951); *Chem. Abstr.*, **46**, 4546 (1952) and earlier references.

base (pK_b 11.9) in that only one nitrogen atom is titratable under the conditions used. The ultraviolet spectrum (λ_{max} 256 mμ, log ϵ 4.30; 325 mμ, log ϵ 4.43) is typical for indoles substituted in the 2-position by an aryl group.[4]

Chemical evidence for the presence of the 3-phenylimidazole ring in both I and II was obtained by the isolation of benzoic acid after alkaline hydrolysis of the respective methiodides.[5] The base (I) is not reduced by sodium borohydride; Child and Pyman found II to be resistant to the action of mild chemical reducing agents.

The base (I) melts at 310° and is only slightly soluble in ordinary solvents; the infrared spectrum in a Nujol mull or potassium bromide disk does not show an absorption band in the 3-μ region (N—H), but there is a complex series of bands between 3.1 and 3.8 μ that could include a displaced N—H band in addition to the absorption from a variety of C—H stretching vibrations. The physical behavior and the infrared spectrum of the imidazo-β-carboline can be interpreted on the assumption of strong intermolecular hydrogen bonding.

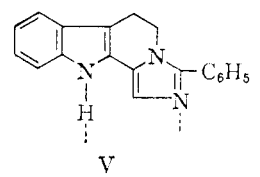
An alternative formulation (IVa or tautomer b)[6] for the condensation product $C_{19}H_{15}N_3$ does not provide a satisfactory model for the titration results. Although IVa would show no N—H band in the infrared, IVa or IVb would be diacidic whereas the base is clearly monoacidic. Spectroscopically IV should show the absorption characteristics of an acylindole in the ultraviolet region,[7] and the azomethine groups of IV would be reduced by sodium borohydride.

Intermolecular hydrogen bonding involving the N—H bond of pyrrole and indole derivatives has long been recognized. In particular the frequency of the N—H stretching vibration has been shown to be considerably lowered by the formation of a complex between pyridine and pyrrole.[8] The basic imidazole ring should be capable of similar interaction with pyrrole N—H group. More recently it has been reported that imidazole, 1,3,4-triazole, and tetrazole, as solids and in concentrated solutions, do not show normal infrared absorption for the N—H stretching frequency, and Otting has proposed that the compounds possess ionic structures under these conditions.[9] The same general behavior has been confirmed for simple imidazole derivatives from a comparative study of the Raman and infrared spectra employing N-deuterated derivatives.[10]

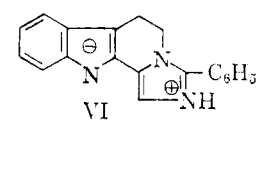
Although I does not possess a normal N—H band in the infrared, deuterium exchange resulted in the appearance of a new band at 4.44 μ corresponding to the replacement of N—D for N—H in I.

The extreme case of interaction between the pyrrolic N—H and the imidazole nitrogen can be represented by the dipolar form (VI) in which proton transfer between the acidic and basic centers is substantially complete. A choice between V and VI cannot be made from examination of the infrared spectrum of the base alone, but the behavior of the base on methiodide formation is more in accord with the formulation of the base as V. The infrared spectrum of the methiodide (VII) possesses a band at 2.98 μ that indicates methylation has occurred on the imidazole ring of I (or V) and not on the pyrrole nitrogen of the dipolar form VI. The further observation that both the hydrochloride and methiodide salts melt lower than the parent base is probably a reflection of the strength of the hydrogen bonding in I.

3-Phenyl-5,6-dihydroimidazo[5,1-*a*]-β-carboline (I) was found to have no significant biological activity in a series of assays.[11]



V



VI

In the imidazo[5,1-*a*]isoquinoline series the 1-methyl derivative (II. R = CH_3) was prepared from ethyl 2-benzamidopropanoate and homoveratrylamine. The structural assignment (II. R = CH_3) for the condensation product is supported by the synthetic method, the analysis, derivatives, and the similarity of its ultraviolet absorption spectrum to II (R = H).

Experimental[12]

(3-Indolyl)ethylhippuramide (III).—A mixture of 14 g. of tryptamine and 20 g. of ethyl hippurate was heated at reflux temperature for 6 hr., cooled, and the solid was dissolved in ethanol. From this solution there was slowly deposited 16 g. (57%) of the amide as colorless crystals, m.p. 180–181°; λ_{max}^{EtOH} 233 (log ϵ 4.64) and 280 mμ (log ϵ 3.77), infrared spectrum (Nujol): 2.94, 3.00, 5.95, 6.08 μ. The amide gave a red-purple color in an Erhlich test.

Anal. Calcd. for $C_{19}N_{19}O_2$: C, 71.01; H, 5.96; N, 13.07. Found: C, 71.01; H, 6.00; N, 13.09.

(4) (a) B. Witkop, *J. Am. Chem. Soc.*, **75**, 3363 (1953); (b) R. B. Carlin, J. G. Wallace, and E. E. Fisher, *ibid.*, **74**, 990 (1952); (c) V. Prelog, *Helv. Chim. Acta*, **31**, 588 (1948); (d) C. E. Blades, and A. L. Wilds, *J. Org. Chem.*, **21**, 1013 (1956); (e) J. M. Bruce, *J. Chem. Soc.*, 360 (1960); (f) M. J. Kamlet and J. C. Dacons, *J. Org. Chem.*, **26**, 220 (1961).

(5) (a) K. Hofmann, "Imidazole and its Derivatives," Part I, Interscience, New York, 1953, p. 50. (b) B. R. Brown and D. White, *J. Chem. Soc.*, 1589 (1957).

(6) For examples of ring closure by condensation of acyl groups on the indole nitrogen see G. Hahn and A. Hansel, *Ber.*, **71**, 2163 (1938); T. Wieland and E. Neeb, *Ann.*, **600**, 161 (1957); A. F. Kiang, F. G. Mann, A. F. Prior, and A. Topham, *J. Chem. Soc.*, 1319 (1956).

(7) Strychinone exhibits λ_{max} (log ϵ) at 246 (4.15), 270 (3.92) and 294 mμ (3.72); *cf.* R. B. Woodward, W. J. Brehm, and A. L. Nelson, *J. Am. Chem. Soc.*, **69**, 2250 (1947).

(8) M. L. Josien and N. Fuson, *J. Chem. Phys.*, **22**, 1169 (1954); S. N. Vinogradov and R. H. Linnell, *ibid.*, **23**, 93 (1955).

(9) W. Otting, *Chem. Ber.*, **89**, 2887 (1956).

(10) D. Garfinkel and J. T. Edsall, *J. Am. Chem. Soc.*, **80**, 3807 (1958).

(11) These tests were kindly performed through the courtesy of the Biological Research Division, The Upjohn Co., Kalamazoo, Michigan.

(12) Melting points are uncorrected.

3-Phenyl-5,6-dihydroimidazo[5,1-*a*]-β-carboline (I).—To 14 g. of (3-indolyl)ethylhippuramide suspended in 200 ml. of refluxing toluene was added 75 ml. of phosphoryl chloride in 100 ml. of toluene over a period of 20 min., and the mixture was allowed to stand overnight. The toluene layer was decanted from the dark residue which was then treated with ice water and made basic with excess ammonium hydroxide. The reaction product was broken up, filtered, and washed with water. The damp solid was dissolved in pyridine mixed with ethanol, and from this dark brown solution a total of 9.4 g. (76%) of golden prismatic crystals was obtained in several crops. Recrystallization from either pyridine or dimethylformamide gave colorless crystals, m.p. 309–310°; λ_{max}^{EtOH} 325 (log ε 4.43) and 256 mμ (log ε 4.30). The pK_b was found to be 11.9 by potentiometric titration.[13] This product gave a faint red color in the pine-splinter test, a negative Ehrlich test; chromic acid oxidation in acetic acid gave a red-brown color that rapidly changed to a brown suspension.

Anal. Calcd. for $C_{19}H_{15}N$: C, 79.97; H, 5.30; N, 14.73; mol. wt., 285. Found: C, 79.86; H, 5.45; N, 14.61; mol. wt. (Rast), 315.

A summary[11] of the biological screening of 3-phenyl-5,6-dihydroimidazo[5,1-*a*]-β-carboline shows that the acute LD_{50} in mice was slightly greater than 1000 mg./kg. (+100–50%) by intraperitoneal injection; it was inactive in the following assays: antiparasitic—*T. vaginalis, E. histolytica, N. muris (in vitro). N. muris (in vivo)*; antiviral—vaccinia and polio (tissue culture); hypertension—DOCA hypertensive rat; evipal potentiation.

Orally the compound produced a mild diuresis in rats which was not, however, of sufficient magnitude to justify further study.

The hydrochloride of the carboline base was obtained by refluxing I in 40% (by volume) hydrochloric acid. It was recrystallized from methanol as pale yellow crystals, m.p. 298° dec.; the infrared spectrum showed a weak band at 2.97 μ.

Anal. Calcd. for $C_{19}H_{16}N_3Cl$: C, 70.91; H, 5.01; N, 13.05. Found: C, 70.60; H, 5.30; N, 12.84.

3-Phenyl-5,6-dihydroimidazo[5,1-*a*]-β-carboline Methiodide.—A solution of 0.2 g. of the base in 50 ml. of hot methanol was treated with excess methyl iodide, and the mixture was refluxed 8 hr. and allowed to crystallize overnight. Pale yellow needles of the methiodide, m.p. 298–300° dec., were obtained quantitatively.

Anal. Calcd. for $C_{20}H_{18}N_3I$: C, 56.22; H, 4.25; N, 9.84. Found: C, 56.27; H, 4.46; N, 9.90.

Attempts to prepare the methiodide in chloroform solution gave deep purple crystals, m.p. 281–282°, of ill-defined composition.

Deuterium Exchange Reaction with I.—A sample of 0.10 g. of imidazo-β-carboline base (I) was refluxed 24 hr. with 3 ml. of deuterium oxide and 2 ml. of ethanol. The liquid was evaporated and replaced by an additional 3 ml. of deuterium oxide. After refluxing 24 hr. longer this suspension was filtered, and the imidazo-β-carboline was recovered. The ultraviolet spectrum of the base was unchanged. The infrared spectrum (KBr) showed a medium intensity band at 4.44 μ, assigned to ν_{N-D}.

Alkaline Hydrolysis of 3-Phenyl-5,6-dihydroimidazo[5,1-*a*]-β-carboline Methiodide.—A suspension of 1.5 g. of imidazo-β-carboline methiodide (VII) in 20 ml. of ethanol, 2 ml. of water, and 8 g. of potassium hydroxide was refluxed 16 hr. The cooled mixture was diluted to 75 ml. and extracted several times with a 2:1 (by volume) solution of ether–dichloromethane. The yellow aqueous layer was acidified and 2.5 g. of a rust-colored solid, m.p. 118–120°, was obtained. This was washed with sodium sulfite solution and recrystallized from hot water as colorless crystals, m.p. 121–122°; melting point was unchanged on admixture with benzoic acid.

The organic extracts were concentrated and the residue was redissolved in ethanol. From this solution there was obtained 0.6 g. of a dark brown amorphous solid, m.p. 228° dec. Further attempts to purify the solid by crystallization or by preparation of acid salts were unsuccessful.

Ethyl 2-Benzamidopropanoate.—A suspension of 31 g. (0.2 mole) of *dl*-alanine ethyl ester hydrochloride in 140 ml. of benzene was treated with 28 g. (0.2 mole) of benzoyl chloride, and to the stirred mixture 25 g. of anhydrous sodium carbonate was added in small portions. The mixture was heated to reflux temperature for 15 min. and stirred 3 hr. longer. The reaction mixture was filtered and the solid was washed with benzene and acetone. The filtrate was concentrated, and the gelatinous precipitate was redissolved in methanol from which 36 g. of the product was obtained as colorless crystals, m.p. 75–76° (lit.,[14] m.p. 76–77°).

N-(3,4-Dimethoxyphenylethyl)-2-benzamidopropanamide.—A mixture of 22 g. (0.1 mole) of ethyl 2-benzamidopropanoate and 18 g. (0.1 mole) of 3,4-dimethoxyphenylethylamine was refluxed for 6 hr. The reaction mixture was triturated with a solution of ether and methanol and finally crystallized to yield 19 g. of amide, m.p. 90–110°. Recrystallization from methanol–ether gave colorless crystals, m.p. 112–113°.

Anal. Calcd. for $C_{20}H_{24}N_2O_4$: C, 67.40; H, 6.99; N, 7.86. Found: C, 67.74; H, 6.90; N, 7.81.

1-Methyl-3-phenyl-8,9-dimethoxy-5,6-dihydroimidazo[5,1-*a*]isoquinoline.—To 16 g. of N-(3,4-dimethoxyphenylethyl)-2-benzamidopropanamide in 200 ml. of refluxing dry toluene was added 90 ml. of phosphoryl chloride in 100 ml. of toluene during the course of 1 hr. The mixture was stirred 3 hr. longer without heating and hydrolyzed overnight. The aqueous layer was treated with charcoal and made basic with ammonium hydroxide. A light brown gummy substance separated that was dissolved immediately in alcohol, but failed to crystallize directly. The alcoholic solution was treated with hydrochloric acid, and 1.5 g. of crystals was collected. This was recrystallized from alcohol to give colorless prisms, m.p. 252–253° dec.

Anal. Calcd. for $C_{20}H_{21}N_2O_2Cl$: C, 67.31; H, 5.93; N, 7.85. Found: C, 67.08; H, 6.30; N, 7.68.

The free base (II. R = CH_3) was obtained by dissolving the hydrochloride in water and treating the solution with 10% sodium hydroxide solution. The base, recrystallized from a mixture of alcohol–ligroin, melted at 160–161°; λ_{max} (log ε) 314 mμ (4.34); λ_{Min} 267 mμ (log ε 3.99).

Anal. Calcd. for $C_{20}H_{20}N_2O_2$: C, 74.97; H, 6.29; N, 8.75. Found: C, 74.91; H, 6.46; N, 8.88.

The original alcohol solution gave a picrate, m.p. 203–204°.

Anal. Calcd. for $C_{26}H_{23}N_5O_9$: C, 56.83; H, 4.22; N, 12.70. Found: C, 56.84; H, 4.47; N, 12.75.

3-Phenyl-5,6-dihydro-8,9-dimethoxyimidazo[5,1-*a*]isoquinoline (II).—This compound was prepared by the method described by Child and Pyman.[1] The pure compound melted at 186–187° (lit.,[1] m.p. 187°); λ_{max} (log ε) in ethanol: 312 mμ (4.42); λ_{min} 262 mμ (log ε 3.99).

The methiodide of II was obtained by refluxing II with excess methyl iodide and recrystallized from methanol as colorless crystals, m.p. 253–255° (lit.,[1] m.p. 255°).

Alkaline Hydrolysis of 3-Phenyl-5,6-dihydro-8,9-dimethoxyimidazo[5,1-*a*]isoquinoline Methiodide.—A solution of 12 g. of potassium hydroxide in 22 ml. of ethanol and 6 ml. of water was added to 4.1 g. of the methiodide of II, and the mixture was refluxed 24 hr. The cooled liquid separated into two layers that were evaporated to an oily residue. The addition of water left an inorganic solid that was removed by filtration and washed with ether. The filtrate was extracted three times with ether and the extracts combined with the ether from the washing. The aqueous solution was acidified with hydrochloric acid and cooled to give colorless needles, wt. 0.8 g., m.p. 121–122°. This was identified as benzoic acid by mixture melting point.

(13) J. S. Fritz, *Anal. Chem.*, **25**, 407 (1953).

(14) K. Brenzinger, *Z. physiol. Chem.*, **16**, 580 (1877).

Evaporation of the ether solutions gave a red oil that failed to crystallize and gave a picrate that did not melt below 350°.

The Morpholine-Iodophenylacetylene Adduct or Charge-Transfer Complex. Formation and Conversion to N-Styrylmorpholine[1]

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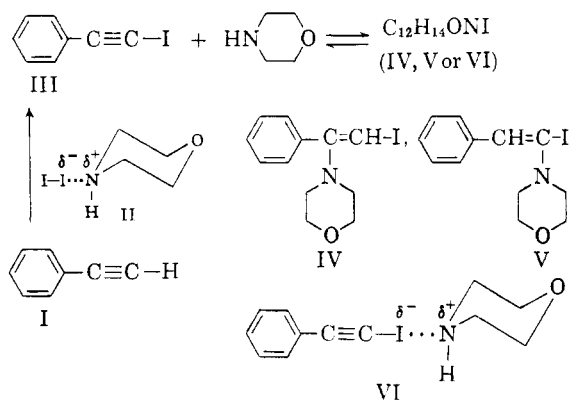
Received August 5, 1961

We have found that morpholine and iodophenylacetylene (III) (1-iodo-2-phenylethyne) react exothermically to form a solid 1:1 adduct. The compound crystallized from petroleum ether in the form of flat, colorless needles or plates, m.p. 75–76° dec. and yielded analytical data agreeing well with the formula $C_{12}H_{14}ONI$. The substance is readily accessible; it can be made directly from phenylacetylene (I) by treating that compound with the iodine-morpholine complex (II)[3,4] and excess morpholine in methanol solution at room temperature. The second method of preparation probably involves intermediate formation of iodophenylacetylene (III). We have made a preliminary investigation of the chemistry of the adduct with the purpose of elucidating its structure. However, the behavior of the compound, although interesting, has been such as to render structure determination by chemical methods somewhat inconclusive.



The most characteristic feature of the behavior of the adduct was its ease of decomposition to morpholine and iodophenylacetylene. It was this property which made it difficult to reach secure conclusions regarding the structure of the substance. When merely suspended in water for several hours at room temperature it dissociated. The morpholine dissolved in the water, leaving iodophenylacetylene as a layer of oil. Catalytic hydrogenation over a Raney nickel catalyst performed in excess morpholine as the solvent resulted in the formation of ethylbenzene. Reduction with lithium aluminum hydride in ether yielded phenylacetylene. It was expected that if the adduct had structure IV or V these reduction procedures would lead to stable products in which the moiety derived from phenylacetylene would be linked to the morpholine nitrogen. The fact that this expectation was not fulfilled may mean that the parts of the adduct are not linked by a carbon-nitrogen bond.

The infrared spectrum of the adduct, determined on a Nujol mull to minimize the possibility of dissociation, resembled that expected for a mixture of morpholine and iodophenylacetylene. There was, for example, a band at 3.06 μ which could be assigned to the N—H bond. It was therefore concluded that the adduct could not correspond to formulas IV or V unless such structures would undergo dissociation even when the compound was merely suspended in Nujol. The ultraviolet spectrum, determined in cyclohexane solution, was virtually identical with that of iodophenylacetylene, a result that may reflect dissociation of the adduct in the dilute solution used for the measurement. There is no reason to suppose either that a compound of structure IV or V would have the same ultraviolet spectrum as iodophenylacetylene or that it would be so unstable as to dissociate almost completely upon being dissolved in cyclohexane.[5]

The nuclear magnetic resonance spectrum (60 Mc.), likewise measured on a cyclohexane solution, was entirely blank in the region between the phenyl pattern at τ = 2.50 to 2.90 p.p.m. and the morpholine A_2B_2 pattern at τ = 6.40 to 7.35 p.p.m.; the one-proton singlet due to vinyl hydrogen expected from structure IV or V was either entirely absent or else hidden by the phenyl pattern. The latter possibility is unlikely; the n.m.r. data provided no support for structure IV or V.

The properties of the morpholine-iodophenylacetylene compound are reminiscent of those reported by Nef[6] for the aniline-iodophenylacetylene

(1) Based on a portion of a thesis submitted by Jack R. Kirchner in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology, June, 1958.

(2) DuPont Fellow in Chemistry, 1957–1958.

(3) R. V. Rice and G. D. Beal, U. S. Patent, 2,290,710 (July 21, 1943); *Chem. Abstr.*, **37**, 502 (1943).

(4) For other reactions of the iodine-morpholine complex see (a) P. L. Southwick and D. R. Christman, *J. Am. Chem. Soc.*, **74**, 1886 (1952); (b) **75**, 629 (1953). Formula II represents the compound as a charge-transfer complex. It was pointed out previously (ref. 4a) that in some of its reactions the complex may be regarded as equivalent to a hydroiodide of N-iodomorpholine.

(5) If it could be assumed that in excess morpholine as the solvent the same 1:1 compound would exist, then it could be concluded that the substance probably did dissociate in the cyclohexane solution used for the ultraviolet measurement. The ultraviolet spectrum in morpholine solution shows a maximum at 264 mμ, ϵ 20,900, whereas the 1:1 compound (or iodophenylacetylene) has its strong absorption at 247 mμ, ϵ 20,500, in cyclohexane. Solvent absorption obscured any absorption which might have been evident below *ca.* 260 mμ in the determination made in morpholine solution.

(6) J. Nef, *Ann.*, **308**, 293 (1899).