Action of Alkali on 3-Bromo-2-methyl-4H-pyrido[1,2-a]-pyrimidin-4-one (VI).—A mixture of 8.00 g. of bromo compound (VI) was heated under reflux with 80 ml. of 7% aqueous potassium hydroxide for 45 minutes. The pale yellow solution was cooled. Upon addition of 30 g. of potassium carbonate, an oil separated. The mixture was extracted with five 50-ml. portions of ether. The ethereal extract was dried over potassium carbonate and then treated with hydrogen bromide. A solid separated. The ethereal supernatant liquid was decanted and the residual solid was stirred with 20 ml. of acetone and filtered. The dry hydrobromide of 2-methylimidazo[1,2-a]pyridine (VII) weighed 3.84 g. (54%). After recrystallization from acetone–chloroform, the m.p. was 197–198°.

Anal. Calcd. for $C_8H_9BrN_2$: C, 45.99; H, 4.25. Found: C, 45.25; H, 4.27.

The hydrobromide of 2-methylimidazo[1,2-a]pyridine was treated with excess cold dilute potassium hydroxide. The resulting solution was extracted with several portions of ether. The ethereal extract was dried over potassium carbonate and distilled. 2-Methylimidazo[1,2-a]pyridine (VII) boiled at 262–263° at atmospheric pressure. It solidified when scratched and, upon recrystallization from ether, melted at 45–46°. It is very hygroscopic.

Anal. Calcd. for $C_8H_8N_2$: C, 72.69; H, 6.10; N, 21.19. Found: C, 71.77; H, 6.17; N, 20.56.

Compound VII rapidly forms a methiodide, m.p. 191–192°, when treated with methyl iodide at room temperature.

Anal. Calcd. for $C_9H_{11}IN_2$: C, 39.43; H, 4.05; N, 10.22. Found: C, 39.57; H, 4.46; N, 9.91.

The alkaline mother liquor from the hydrolysis of VI was saturated with carbon dioxide and evaporated to dryness. The residue was extracted with several portions of boiling absolute ethanol. Evaporation of the ethanol, extraction of the resulting residue with ethanol–isopropyl alcohol and re-evaporation to dryness yielded 2.15 g. (30%) of the potassium salt of VIII. A 10 *N* sulfuric acid solution was added dropwise to a solution of 1.20 g. of the potassium salt in 50 ml. of absolute ethanol until the solution was neutral to congo red paper. The resulting mixture of liquid and solid was heated to boiling and filtered. The precipitate was extracted with two 25-ml. portions of boiling absolute ethanol. The ethanolic solutions were combined, concentrated and cooled to give 0.69 g. of 2-methylimidazo[1,2-a]-pyridine-3-carboxylic acid (VIII). The compound decomposed at about 185° with evolution of gas. The decomposition point is largely dependent upon the rate of heating.

Anal. Calcd. for $C_9H_8N_2O_2$: C, 61.36; H, 4.58; N, 15.90. Found: C, 61.33; H, 4.31; N, 15.81.

Approximately 0.1 g. of VIII was heated above the decomposition temperature until gas evolution ceased. The residual liquid was dissolved in ether and treated with hydrogen bromide. A solid separated. The ethereal solution was decanted and the residual solid was washed with a little cold acetone and then recrystallized from acetone. The product melted at 197–198°. Its melting point was not depressed when mixed with a sample of the hydrobromide of VII prepared as described above.

3-Bromo-2-chloro-4H-pyrido[1,2-a]pyrimidin-4-one.—A mixture of 3.3 g. of 2-chloro-4H-pyrido[1,2-a]pyrimidin-4-one,[4] 40 ml. of carbon tetrachloride and 3.5 g. of NBS was heated under reflux with stirring for 30 minutes. The 3-bromo compound crystallized from solution as it was formed. The mixture was filtered and the product was washed with water, dried and concentrated to give a small additional yield. The combined solids were recrystallized from chloroform–ethanol to yield 4.3 g. (90%) of colorless needles, m.p. 225–228°.

Anal. Calcd. for $C_8H_4BrClN_2O$: C, 37.02; H, 1.55. Found: C, 37.26; H, 1.54.

3-Bromo-4H-pyrido[1,2-a]pyrimidin-4-one (XI).—To 40 ml. of carbon tetrachloride was added 1.46 g. of pyridopyrimidone and 1.92 g. of N-bromosuccinimide. The mixture was heated under reflux with stirring for 30 minutes. The product was isolated as described for compound VI. Upon recrystallization from ethanol there was obtained 1.36 g. (60%) of IX, m.p. 133–134°.

Anal. Calcd. for $C_8H_5BrN_2O$: C, 42.69; H, 2.24. Found: C, 42.69; H, 2.24.

Action of Alkali on 3-Bromo-4H-pyrido[1,2-a]pyrimidin-4-one (XI).—A mixture of 0.98 g. of IX and 15 ml. of 5% aqueous sodium hydroxide was heated under reflux for 45 minutes. The solution was cooled and extracted with ether. The ethereal extract was dried over potassium carbonate and evaporated to dryness. The residue, which possessed the odor of 2-aminopyridine, solidified. After two recrystallizations from cyclohexane containing a little carbon tetrachloride, it melted at 56° and its melting point was not depressed upon admixture with authentic 2-aminopyridine.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

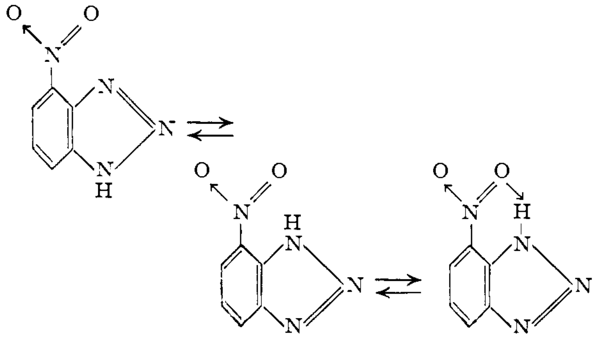
Restriction of Tautomerism in the Triazole System by Hydrogen Bonding. The Case of 4(7)-Nitrobenzotriazole[1]

BY NORMAN L. MILLER AND E. C. WAGNER

RECEIVED SEPTEMBER 2, 1953

Comparative study of the isomeric nitrobenzotriazoles showed the vicinal isomer, 4(7)-nitrobenzotriazole, to be the more volatile, the more rapidly reduced polarographically, the weaker acid, and to be less associated in solution. These characteristics are attributed to existence of chelation in 4(7)-nitrobenzotriazole; as a consequence there is a corresponding restriction of the tautomerism of the benzotriazole system. The results of catalytic hydrogenation did not (as in earlier studies of analogous systems) parallel those of polarographic reduction, indicating the need for caution in the interpretation of results obtained for such systems by catalytic hydrogenation. The ultraviolet absorptions of the two nitrobenzotriazoles likewise proved to be non-committal with respect to chelation in the vicinal isomer.

This paper reports the results of the extension to the 1,2,3-triazole system, represented by the isomeric nitrobenzotriazoles, of the experimental methods used previously to secure inferential evidence for the restriction of tautomerism in other and analogous systems[2-4] owing to involvement of the labile hydrogen in chelation. Of the two nitrobenzotriazoles the 4(7)-nitro isomer has a structure that appears to permit chelation



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(1) Paper constructed from the Ph.D. thesis of Norman L. Miller, University of Pennsylvania, 1953.

(2) M. E. Runner, M. L. Kilpatrick and E. C. Wagner, THIS JOURNAL, **69**, 1406 (1947).

(3) J. L. Rabinowitz and E. C. Wagner, *ibid.*, **73**, 3030 (1951).

(4) M. E. Runner and E. C. Wagner, *ibid.*, **74**, 2529 (1952).

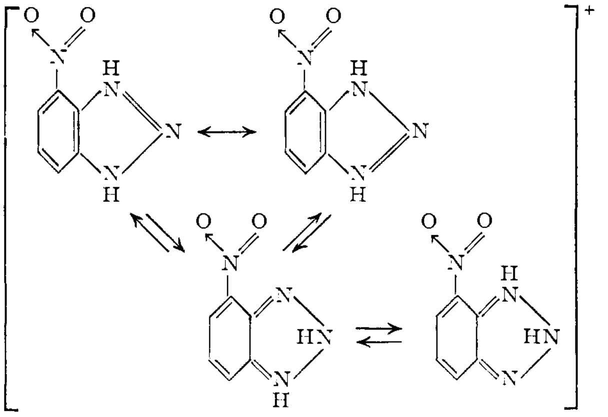
To whatever extent chelation is operative there are to be expected alterations in the character of the nitro group and in properties attributable to the labile hydrogen, *viz.*, acidity, solvation and associative and mesohydric effects. The isomeric 5(6)-nitrobenzotriazole is not capable of chelation, and should show the normal properties of the nitro group and of the triazole structure. Results of six experimental approaches, conducted comparatively with 4(7)-nitrobenzotriazole (I) and 5(6)-nitrobenzotriazole (II), are outlined below.

1. **Volatility.**—Comparative tests showed that 4(7)-nitrobenzotriazole is more volatile with steam, more volatile from hot solvents, and more rapidly sublimable, than is 5(6)-nitrobenzotriazole. This markedly greater volatility of I can be attributed to chelation, which decreases both association and solvation.[5]

2. **Polarographic Reduction.**—The reduction voltages (half-wave potentials) of the isomeric nitrobenzotriazoles and, for comparison, of nitrobenzene (III), were determined polarographically in water at *p*H values of 5.29, 6.24, 7.00 and 8.04, maintained by Sörensen phosphate buffers.[6] As with the nitrophenyl phenyl acetamidines,[2] the nitrobenzimidazoles[3] and the nitroacetanilides,[4] the ionic and molecular states of the nitrobenzotriazoles may be responsive to the *p*H of the solution. As chelation in I must be maximal under neutral conditions (being impossible in presence of alkali sufficient to withdraw the essential hydrogen, and being probably decreased or excluded by acidity sufficient to force acceptance of a proton), attention is directed especially to results obtained near neutrality.[9] Actually the conditions within the *p*H range employed appear to have caused no pronounced effect upon the reduction potentials for, as shown in Table I, compound I is more readily reduced than II or III, throughout the *p*H range stated, by about 0.10 (± 0.02) volt. Except at *p*H 8.04, at which all three compounds are less readily reduced than at lower *p*H values, II and III are reduced at about the same potential, suggesting that in both compounds the nitro group is in normal state. The easier reduction of I is consistent with the view that chelation, involving the labile hydrogen of the triazole system and an oxygen of the nitro group, modifies the character of the latter and makes it more susceptible to polarographic reduction (Table I). Calculation indicated that four-electron reductions had occurred (Table II).

Neutral: Shown above

Acid (chelation is probably excluded by acidity[7]):



Alkaline:

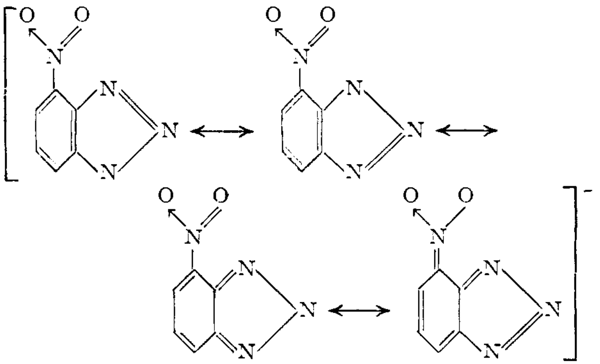


TABLE I

CHANGE OF $E^1/_2$ FOR 5(6)-NITROBENZOTRIAZOLE (II), 4(7)-NITROBENZOTRIAZOLE (I) AND NITROBENZENE (III). CHANGE OF $\Delta E^1/_2$ WITH *p*H.

*p*H	Nitro compd. reduced	$E^1/_2$ at 25° (v.) ± 0.01	$\Delta E^1/_2$, $E^1/_2\text{II} - E/_2\text{I}$ ±0.02	$\Delta E^1/_2$, $E^1/_2\text{III} - E^1/_2\text{I}$ ±0.02
8.04	II	−0.74	0.11	0.04
	I	− .63		
	III	− .67		
7.00	II	− .63	.10	.10
	I	− .53		
	III	− .63		
6.24	II	− .53	.06	.11
	I	− .48		
	III	− .59		
5.29	II	− .51	.08	.13
	I	− .43		
	III	− .56		

TABLE II

DIFFUSION CURRENT AND NUMBER OF ELECTRONS AT 25°

	Nitrobenzene	4(7)-Nitrobenzotriazole	5(6)-Nitrobenzotriazole
Approx. diffusion current, μa.	2.8	2.8	2.8
Approx. *p*H	7	7	7
Approx. diffusion constant from Ilkovic eq., $D \times 10^{-5}$	0.75	0.77	0.75
Approx. diffusion constant from McBain cell, $D \times 10^{-5}$	.72	.76	.77
Time in sec. using McBain cell, $t \times 10^5$	.360	.432	.432
C in μa. for the McBain cell	.56	.90	.83
C' in μa. for the McBain cell	2.00	2.62	2.39
Calcd. electrons involved	4	4	4

3. **Catalytic Hydrogenation.**—Comparative hydrogenations of I and II in ethanol, using palla-

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[5] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 332.

[6] W. M. Latimer and J. H. Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Company, New York, N. Y., revised edition, 1940, p. 509.

[7] Ultraviolet absorption results[8] are interpreted to indicate the cation to be in the quinonoid form.

[8] J. E. Fagel and G. W. Ewing, THIS JOURNAL, **73**, 4360 (1951).

[9] Reference 3, p. 3032, footnote 8.

dium-on-carbon as catalyst, a pressure about 10 mm. above atmospheric, and temperatures of 25, 30 and 50°, showed the rate of consumption of hydrogen to be consistently greater for II than for I; under the same conditions benzotriazole absorbed no hydrogen. The average periods for complete reduction are: at 25°, I, 23.9 min.; II, 19.4 min.; at 30°, I, 20.8 min.; II, 16.0 min.; at 50°, I, 18.9 min.; II, 15.3 min. The relationships throughout the reductions are shown in Figs. 1, 2 and 3, which reveal that from the outset II is more rapidly hydrogenated than I. Increase in the amount of catalyst increased the rates for both compounds about equally. With less catalyst compound I absorbed hydrogen more rapidly during the first five minutes, after which the hydrogenation of II, as in all other experiments, was the more rapid. Hydrogenations using platinum oxide or palladium on alumina resulted similarly; with Raney nickel no hydrogenation occurred. The rates of hydrogenation of 1-methyl-6-nitrobenzotriazole and 1-methyl-7-nitrobenzotriazole (neither capable of chelation or tautomerism) were identical with those of II and I, respectively.

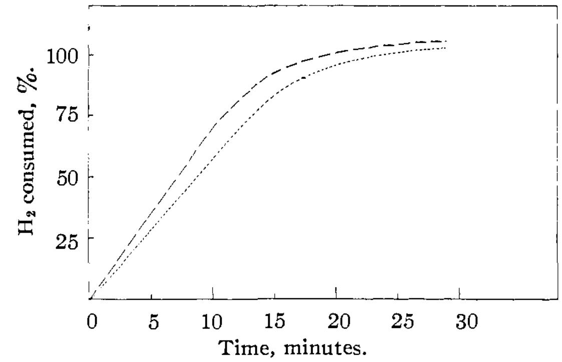

Fig. 1.—Catalytic hydrogenation of 5(6)- and 4(7)-nitrobenzotriazole at 25° using Pd–C catalyst: — — —, 5(6)-nitrobenzotriazole; · · ·, 4(7)-nitrobenzotriazole.

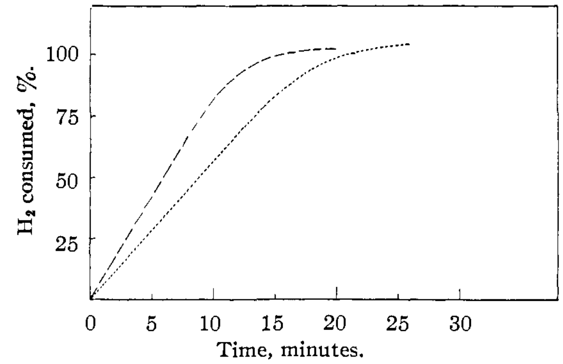

Fig. 2.—Catalytic hydrogenation of 5(6)- and 4(7)-nitrobenzotriazole at 30° using Pd–C catalyst: — — —, 5(6)-nitrobenzotriazole; · · ·, 4(7)-nitrobenzotriazole.

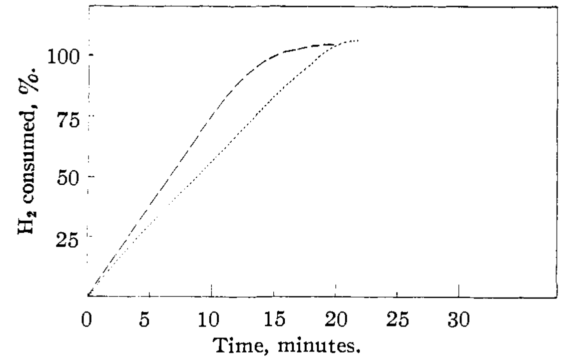

Fig. 3.—Catalytic hydrogenation of 5(6)- and 4(7)-nitrobenzotriazole at 50° using Pd–C catalyst: — — —, 5(6)-nitrobenzotriazole; · · ·, 4(7)-nitrobenzotriazole.

The results for hydrogenation of the isomeric nitrobenzotriazoles, since they are the reverse of those anticipated, were verified by repeated trials with attention to the exclusion of fallacy. They appear to cast doubt upon the validity of conclusions drawn with respect to other compounds[2,3,4] which had yielded the expected results, the isomer capable of chelation in each case being more rapidly hydrogenated, though a hint of irregularity appeared during catalytic hydrogenations of the isomeric nitrobenzimidazoles.[3] The results for hydrogenation of I and II show differences not attributable to chelation in I. They do not necessarily suggest absence of chelation but perhaps a dependence of the rates of catalytic hydrogenation upon undetermined structural, polar or adsorptive influences.

4. **Base Strengths.**—It seems probable that chelation in I would not impair the ability of the triazole system to accept a proton, and that I and II should differ only slightly with respect to base strengths. Experiment confirmed this surmise: potentiometric titrations of aqueous solutions of I, II and also of benzotriazole with standard hydrochloric acid showed the half-equivalent point for I and II to be at *p*H 3.90 and the equivalence point at *p*H 3.65 (Fig. 4).

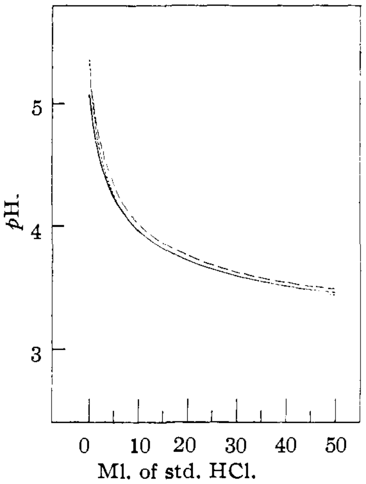

Fig. 4.—Potentiometric titration of 5(6)- and 4(7)-nitrobenzotriazole and benzotriazole with 0.001 *N* hydrochloric acid: —, 5(6)-nitrobenzotriazole and benzotriazole; - - -, 4(7)-nitrobenzotriazole.

Acid Strengths.—It may be assumed that the influence of the nitro group is to increase the acid characters of I and II. In I the effect is exerted from the ortho and meta positions and in II from the meta and para positions; the former effect is probably slightly the stronger. Chelation in I binds the essential hydrogen, so that I is acidic to an extent that reflects the degree of instability of the chelate ring. From these considerations it may be inferred that I possesses an acid character weaker than that of II but perhaps stronger than that of benzotriazole.

The experimentally determined *p*H values obtained by titrating I, II and benzotriazole with standard sodium hydroxide show (Fig. 5) that I is a weaker acid than II by 0.29 of a *p*H unit and that benzotriazole is weaker than I. This difference between I and II cannot reasonably be ascribed to the positional influence of the nitro group, but is believed to be a consequence of chelation, which involves the essential hydrogen and resists its withdrawal as proton.

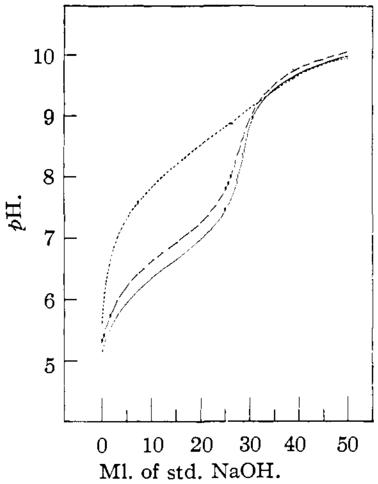

Fig. 5.—Potentiometric titration of 5(6)- and 4(7)-nitrobenzotriazole and benzotriazole with 0.001 *N* sodium hydroxide: —, 5(6)-nitro-; — — —, 4(7)-nitro-; · · ·, benzotriazole.

5. Ultraviolet Absorption.—Figure 6 represents the ultraviolet absorptions of I and II in acid and alkaline solutions in ethanol. Absorptions of the neutral solutions are similar, with maxima for I at 322 and 230 mμ, and for II at 292.5 and 241 mμ, the displacements for the two isomers being attributable to the positions of the nitro groups. In acid solution (0.1 *N* hydrochloric acid, Fig. 6) absorptions were the same as in neutral solution. In this case, since in acid solution the triazole systems of the two isomers I and II become identical,[8] the spectral differences are clearly due to positional effects of the nitro groups. In alkaline solution (0.1 *N* sodium ethoxide) the two isomers show different ultraviolet absorptions (Fig. 6), the maxima for I being at 366 and 233 mμ, and for II at 316 and 258 mμ. Absorptions assignable to the triazole structure[10] are markedly displaced, probably owing to quinonization.

The recorded ultraviolet absorptions present no evidence for chelation, but actually they are merely non-committal, since any effects resulting from chelation may be in regions where they are masked by strong absorptions caused by structural features common to both isomers.

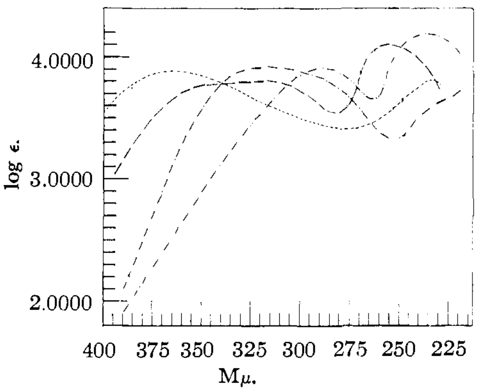

Fig. 6.—Ultraviolet absorptions of 5(6)- and 4(7)-nitrobenzotriazole in ethanol-hydrochloric acid and ethanol-sodium ethoxide solutions: —·—, 5(6)-nitrobenzotriazole, 0.01 *N* HCl in ethanol; ——, 4(7)-nitrobenzotriazole, 0.01 *N* HCl in ethanol; — — —, 5(6)-nitrobenzotriazole, 0.1 *N* NaOEt; - - -, 4(7)-nitrobenzotriazole, 0.1 *N* NaOEt.

6. Degrees of Association of I and II in Solution.—The association of the triazole system,[11] caused by intermolecular sharing of the imino hydrogen, is decreased to an extent related to that of any intramolecular involvement of this hydrogen in chelation. The ability of a nitro group vicinal to the —NH—N=N— system to bind the hydrogen atom was tested by comparative determinations, for I and II, of the association factors (M_x/M_o, the values of which normally increase with concentration. Molecular weight determinations were made cryoscopically in phenanthrene; some other substances with melting points lower and more favorable to both chelation and association were found to be insufficiently good solvents for the purpose. The results are shown in Table III. The value of M_x/M_o for I is nearly unity, the curve relating M_x/M_o and concentration showing only a gentle slope. The association factors for II range from 1.04 (0.01 molal) to 1.22 (0.06 molal). The differences reach about 17%; the errors in the determination do not exceed 3%. It is obvious that in I some influence operates strongly in competition with association; the inference that this is chelation is consistent with similar conclusions long accepted with respect to other compounds similarly tested, *e.g.*, *o*-nitrophenol.

Of the evidence presented above, that of volatility, polarographic reduction, acid strength and association factors permit an apparently valid inference that chelation exists in 4(7)-nitrobenzotriazole. The results of catalytic hydrogenation, which in previous studies[2-4] paralleled those of polarographic reduction, are for the nitrobenzotriazoles reversed, for reasons that are not apparent. As in previous studies, ultraviolet absorptions yielded no evidence interpretable with respect to chelation.

Experimental

Materials.—Benzotriazole was obtained in 75% yield by the method of Damschroder and Peterson[12]; after two crys-

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[10] A. K. MacBeth and J. R. Price, *J. Chem. Soc.*, 111 (1936).

[11] T. G. Heafield and L. Hunter, *ibid.*, 420 (1942).

[12] R. E. Damschroder and W. D. Peterson, *Org. Syntheses*, **20**, 16 (1940).

tallizations from benzene the colorless product melted at 95–95.5° cor. **4(7)-Nitrobenzotriazole** was obtained in 30.9% yield by nitration of benzotriazole using the procedure of Fries, Güterbock and Kühn.[13] After seven recrystallizations from alcohol the yellow needles melted at 236–237.3° cor. **5(6)-Nitrobenzotriazole** was made from 1,2-diamino-4-nitrobenzene by action of nitrous acid, using the procedure of Zincke, Stoffel and Petermann.[14] The yield was 57%, and the pale yellow product, after five recrystallizations from alcohol, melted at 215–216° cor. **1-Methylbenzotriazole** was obtained by methylation of benzotriazole with methyl sulfate and alkali, using the procedure of Krollpfeiffer, Rosenberg and Mühlhausen.[15] The product, distilled under reduced pressure (yield 13%) and recrystallized from ligroin, melted at 95–96° cor. **1-Methyl-7-nitrobenzotriazole** was made by nitration of 1-methylbenzotriazole by the procedure of Fries, Güterbock and Kühn.[16] After crystallization from alcohol the yellow crystals (32%) melted at 202–203° cor. **1-Methyl-6-nitrobenzotriazole** was made by the procedure of Brady and Reynolds[17] from 5(6)-nitrobenzotriazole by methylation with methyl sulfate and alkali. It was crystallized alternately from alcohol and benzene, leaving a yield of 22%; after five recrystallizations from alcohol the pure product melted at 185–186° cor.

Volatility Tests. 1. **Sublimation:** In comparative trials weighed portions of I and II were heated at 120° for one hour and under reduced pressure (12 mm.) in a sublimation apparatus, and the weight of compound volatilized was determined. In typical experiments 0.0339 g. of I lost 0.0101 g., and 0.0332 g. of II lost only 0.0010 g. The sublimed materials had the same melting points as before. Other experiments confirmed these results, and it is shown that under the conditions used I sublimes 10 times as rapidly as II. 2. **Steam Distillation:** Weighed samples of 0.5 g. of I or II, dissolved in 200 ml. of water, were separately submitted to steam distillation in a conventional apparatus. The amount of I found in the first 25 ml. of distillate (collected in 20 minutes) was found to be 0.26 g. By the same procedure II proved to be not volatile with steam. Incidental observations during recrystallizations from ethanol showed I but not II to be rather freely volatile in alcohol vapor from the hot solution, the former appearing as a deposit on the walls of the beaker and on the cover glass. This material was identified as I by m.p.

Polarographic Reduction.—Measurements were made with a Leeds and Northrup Electro-Chemograph, type E, model no. 62200, operated at damping position #1[18] and at the 5-ampere range. Calibration of the dropping mercury electrode (an 8-cm. section of Corning marine barometer glass) yielded for $m^{2/3}t^{1/6}$ the value 1.80 mg.$^{2/3}$sec.$^{1/2}$ for a 70 cm. head of mercury. Measurements were made at 25 ± 0.1°.

The H-type electrolysis cell[19] was prepared for use by bubbling nitrogen (purified by the method of Meites and Meites[20]) for 20 minutes through the lower nitrogen line to remove oxygen, after which the nitrogen was passed through the upper line, to avoid disturbance of the drop formation of mercury[21]; the current of nitrogen over the surface of the liquid served to prevent admission of air. This cell was connected with a permanent external anode with a sintered glass disc of fine porosity and of 10 mm. diameter.

The H-type cell with S.C.E. contained in the anode chamber (from below upward) successive layers of (1) pure mercury, (2) calomel, mercury and some solid potassium chloride, and (3) saturated aqueous potassium chloride. The platinum electrode, held firmly by a rubber stopper, was so placed that the platinum wire was in contact with the mercury. When not in use the cell was kept filled with saturated potassium chloride solution.

The buffer solution of *p*H 7 (25°) was prepared by diluting National Technical Laboratory concentrated buffer solution with 24 parts of distilled water. The other (phosphate) buffers, of *p*H 5.29, 6.24 and 8.04, were prepared according to Sörensen.[6] The several values were checked by testing the buffers with a Beckman glass-electrode *p*H meter (Model G), itself standardized against National Technical Laboratory concentrated buffer solution.

The buffered solutions of the nitrobenzotriazoles, prepared in a 50-ml. volumetric flask immediately before use consisted of 10 ml of 0.1 *M* potassium chloride, 10 ml. of the selected buffer solution, and 10 ml. of 0.001 *M* nitrobenzotriazole (0.1641 g. of nitrobenzotriazole in 1 liter of previously boiled and cooled water), and distilled water to the 50-ml. mark. The high ratio of buffer to nitrobenzotriazole (about 100:1) ensured constancy of *p*H during electrolysis.[22,23]

Procedure.—The saturated potassium chloride solution was drained from the electrolysis cell, which was rinsed with some of the buffered solution to be examined. A 10-ml. aliquot of the buffered sample solution was pipetted into the electrolysis chamber, and 0.5 ml. of 0.2% gelatin solution was added.[24] The bubbler through which the stream of nitrogen passed just prior to entering the electrolysis cell was charged with 10 ml. of a solution of the same composition as that in the cell. The tip of the capillary was kept about 3 mm. below the surface of the buffered solution in the cell. The system was flooded with a stream of nitrogen for 20 minutes before the solution was polarized and before readings were taken. Each examination was repeated at least three times, with both forward and reversed polarization and the average half-wave potentials were recorded; individual values differed from the average by 0.01 v. or less. Residual current curves were obtained in the same manner, the solution in the cell containing 10 ml. of water instead of the sample solution. The half-wave potential data appear in Table I. The **diffusion coefficient** was estimated at room temperature (*ca.* 25°), with corrections to 25°, using a cell of the type described by McBain and Liu.[25] For the calculation there was employed the simplified equation derived by Runner[26] from that of King and Cathcart.[27] The cell constant, determined by use of nitrobenzene, was 0.55; the head of mercury and the drop time were constant, so that one calibration of the dropping mercury electrode sufficed. A preliminary diffusion period of 6 to 12 hours assured equilibrium with the fritted membrane.

The extent of reduction was estimated by use of the Ilkovic equation[28]; results appear in Table II. The four-electron reduction indicated for nitrobenzene and the isomeric nitrobenzotriazoles is not readily explained. Interference by the gelatin added to suppress maxima has been suggested,[29] but the effects claimed (shifting of half-wave potential and decrease in diffusion current) do not appear to account for the discrepancy between the four-electron reductions calculated and the six-electron reductions expected.

Catalytic Hydrogenation.—The apparatus was the same as that used in similar work by Rabinowitz and Wagner.[30] Reductions were effected in a 50-ml. erlenmeyer flask seated above a magnetic stirring mechanism housed under a liquid-tight elevation in the floor of a constant temperature bath, by which the temperature was maintained constant within ±0.1°. Gas volumes were read to 0.1 ml., and in all experiments the stirrer was operated as nearly as possible at the same rate.

The weighed sample (0.1641 g.) of I or II was introduced into the hydrogenation flask containing the magnetized stirring bar, the weighed catalyst was added, and then 25 ml. of absolute ethanol. In most of the trials the catalyst was 5% palladium-on-carbon, prepared as directed by

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Hartung[31] and stored over solid potassium hydroxide in a desiccator; the catalysts were used in amounts of 0.025, 0.05 or 0.10 g., but in all comparative reductions of I and II the same weights of catalysts were used. With the flask supported in the constant temperature bath and above the stirring impeller the stirrer was operated for several minutes to ensure dissolution of the sample and thermal uniformity of the suspension, and to promote maximal adsorption on the catalyst. Stirring was interrupted, and the flask was connected to the delivery tube of the hydrogen system and was flooded with hydrogen, and then evacuated several times to remove air, and finally was filled with hydrogen under 10 mm. pressure. The stirrer was put into operation and the time and the reading of the hydrogen buret were recorded. The pressure was maintained at 10 mm. by frequent adjustments, and readings of time and volume of hydrogen consumed were recorded until absorption of hydrogen ceased. The results represented by Figs. 1, 2 and 3 in most cases are averages of those obtained from several runs. Hydrogenations of I using palladium-on-charcoal at 25, 30 and 50°, and using palladium-on-alumina or platinum oxide at 30°, resulted similarly. Hydrogenations of 1-methyl-4-(7)-nitrobenzotriazole and 1-methyl-5(6)-nitrobenzotriazole, using palladium-on-carbon, were found to occur at rates identical with those of I and II, respectively.

Reduction of the nitro group in all cases was complete, as was shown by isolation of the reduction products and identification as the corresponding aminobenzotriazoles by comparing the products and also their acetyl derivatives with specimens independently prepared.[13]

Acid-Base Strengths by Potentiometric Titration.—Titrations of 25-ml. portions of 0.001 M solutions of I, II and benzotriazole in water were made with 0.001 N hydrochloric acid and 0.001 N sodium hydroxide with the aid of a Beckman pH meter with calomel half-cell and glass electrode. Data for the three compounds, representing for each the averaged results of repeated trials, are plotted (volume of standard solution *vs.* pH) as Figs. 4 and 5, which reveal that they differ scarcely at all in base strengths (Fig. 4), but that I is a weaker acid than II by 0.29 pH unit throughout most of the titration (Fig. 5). The pH values at half- and full-equivalence are

	Half-equivalence pH	Equivalence pH
I	6.77	7.75
II	6.48	7.46
Benzotriazole	8.00	8.73

Ultraviolet Absorption.—The spectra of the isomeric nitrobenzotriazoles were mapped by use of a Beckman quartz spectrophotometer with matched quartz cells. The solvent in all cases was ethanol; for observations in acid medium the alcohol was 0.01 N in hydrochloric acid, and for those in alkaline medium it was 0.01 N with respect to sodium ethoxide. The large amounts of acid or base relative to sample assure effective buffer action. The data, plotted as $m\mu$ *vs.* log E, yield the curves of Fig. 6. The positions of maxima are mentioned in the Discussion.

Degrees of Association.—For determinations of apparent molecular weights of I and II in pure phenanthrene (m.p. 98.5°) the apparatus and procedure were based on those of Auwers[32] as modified by Rabinowitz and Wagner.[3] The rotary magnetic stirrer designed by Rabinowitz[33] proved to be very satisfactory. The freezing-point reading (on the Beckmann thermometer) for the phenanthrene was ascertained by three trials, in which supercooling was held to 0.2° and the temperature range was 0.008°. The freezing point constant was then determined by use of pure triphenylmethane. Readings, each in duplicate, were taken at six concentrations. The averaged results indicated the constant for phenanthrene (for these materials, equipment and manipulations) to be 11.8; the value reported is 12.0.[34]

The apparent molecular weights of I and II were determined at nine concentrations. Measurements for II could not be made above a concentration of about 0.06 molal, owing to evidence of mixed crystal formation. The solution of I in phenanthrene showed a distinct yellow coloration at about 0.1 molal, beyond which point no determination was made. Essential results of the association study are grouped in Table III and present the supporting data.

TABLE III

DEGREES OF ASSOCIATION OF 4(7)- AND 5(6)-NITROBENZOTRIAZOLES IN PHENANTHRENE

Compound	Concn., M	Apparent mol. wt.	Assoc. factor, M_x/M_0	Compound	Concn., M	Apparent mol. wt.	Assoc. factor, M_x/M_0
I 4(7)-	0.011	161.6	0.985	II 5(6)-	0.006	170.7	1.040
	.026	163.2	.995		.012	174.5	1.064
	.033	163.6	.997		.018	177.6	1.082
	.040	163.4	.996		.026	181.2	1.104
	.047	166.3	1.013		.035	185.1	1.128
	.059	162.7	0.992		.042	188.3	1.147
	.072	164.3	1.001		.048	190.2	1.159
	.085	169.5	1.032		.056	195.6	1.192
	.101	168.2	1.025		.065	199.4	1.215

PHILADELPHIA, PENNA.

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