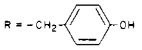
where anticipated (the shift between α-methyls is 0.31 p.p.m. for isopropyl and 0.26 p.p.m. for *sec*-butyl; the shift between β-methyls is ~0.1 p.p.m. for *sec*-butyl and 0.07 p.p.m. for isobutyl; $S—CH_3$ is a sharp singlet at −2.00 p.p.m. The benzylic CH_2 protons are a moderately sharp doublet (8.1 ± 0.2 Hz at −3.92 p.p.m.) for benzyl and broad doublet (7 Hz at −3.90 p.p.m.) for *p*-hydroxy benzyl. Other CH and CH_2 protons in the *R* groups are not seen well because of interference by the ring protons. The acid OH proton was seen in the range −13 to −15 p.p.m. For



the combined OH and COOH proton line was at −13.17 p.p.m.

The spectra of the cyclohexane ring protons give strong evidence for trans placement of the rings fused to it and one strongly preferred conformation. This assignment is based on the general first-order splitting features of groups *A* and *B*, and limits may be placed on other intergroup couplings. The poor resolution of these patterns is attributed readily to high complexity arising from strong coupling between vicinal protons at the ring junctures and weaker long range couplings. A complete analysis of the system was not performed; it is unlikely to be very exact and should not affect the resulting structure assignment.

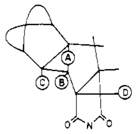
Groups *A* and *B* may be assigned to the CH_2 protons at the prow of the boat form. The distortion of their patterns and common splitting of ~14 Hz is typical of geminal placement, and chemical shifts are reasonable. The *A* protons are assigned as predominantly axial on the basis of their higher shift and implied couplings to *C* and *D* protons—a large coupling to *C* (~ 12 Hz) and smaller coupling to *D* (~2 to 4 Hz) suggests trans placement of *C* to *A* and gauche placement of *D* to *A*. This assignment is consistent with the broad pattern of *C* and "narrow" pattern of *D*. Predominantly equatorial placement of *B* is consistent with its lower shift and smaller couplings to both C and *D*.

Protons *C* and *D* are assigned to those at the junctures with the fused rings, but no choice can be made on the basis of their chemical shifts. The placement of protons *C* trans to *A* and gauche to *B*, while protons *D* are gauche to both *A* and *B* implies that the fused ring to which proton *C* belongs must be predominantly equatorial while the fused ring to which protons *D* belongs must be predominantly axial. Therefore, the rings fused to the central cyclohexane ring must be placed trans to one another.

One would anticipate equatorial placement of the bicycloheptene and axial placement of the anhydride rings rather than the converse, because transannular interaction by the planar imide being axial should be less than having the more bulky chlorinated bicycloheptene ring axial. By this argument, protons *C* would be assigned to being at the juncture with the equatorial bicycloheptene ring and protons *D* at the juncture with the imide ring.

No decision is made with respect to placement of the cyclohexane ring on the bicycloheptene ring—i.e., endo or exo to the double bond. The relative constancy of the ring proton pattern throughout this series of compounds is good indication that this placement is the same for all.

In conclusion the tentative structure assignment is



LITERATURE CITED

(1) Horsfall, J.G., "Principles of Fungicidal Action," pp. 73, 201, Chronica Botanica Co., Waltham, Mass., 1956.

(2) Kenaga, E.E., *Bull. Entomol. Soc. Am.* **12**, 161 (1966).

(3) Roberts, C.W., Haigh, D.H., Rathsack, R.J., J. CHEM. ENG. DATA **12**, 450 (1967).

(4) Soloway, S.B., Damiana, A.M., Sims, J.W., Bluestone, H., Lidov, R.E., *J. Am. Chem. Soc.* **82**, 5377 (1960).

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Some Derivatives of 1,4-Diazabicyclo(2.2.2)octane (Triethylenediamine)

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TRIETHYLENEDIAMINE, or 1,4-diazabicyclo(2.2.2)-octane, was first synthesized in 1942 in low yields by Hromatka (*16*) from the hydrochlorides of the ethanolamines. This cage-type ditertiary amine is characterized by high symmetry, globular structure, high melting point, and contains two exposed nitrogen atoms whose unshared electron pairs are free of steric hindrance. From the unique structure of triethylenediamine stems a number of its interesting chemical, physical, and thermodynamic properties (*13*). The unhindered "lone pair" electrons of the nitrogen atoms of triethylenediamine are responsible for its high nucleophilicity and its catalytic activity in base-catalyzed reactions. With the advent of economical methods of synthesis (*2, 7-9, 17, 18*), triethylenediamine became one of the most efficient (*3, 12, 14, 15, 22*) and most widely used catalysts for the production of urethane foams. The present paper is concerned with some derivatives of triethylenediamine that show the changes in properties and the reactivity of the exposed nitrogen atoms on introducing a methyl group into the triethylenediamine structure.

2-METHYLTRIETHYLENEDIAMINE

Introduction of a methyl group into triethylenediamine destroys its symmetry and produces an asymmetric carbon atom. Thus, 2-methyltriethylenediamine is a liquid in contrast to the more symmetrical triethylenediamine, which is a solid (m.p. 159.8° C.).

2-Methyltriethylenediamine has been synthesized by the catalytic cyclodehydration of hydroxyethylated 2-methylpiperazine (*5, 6*). Purification was accomplished by fractional distillation followed by gas chromatographic separation.

The physical and chemical properties of triethylenediamine and its methyl derivative are compared in Table

1,4-Diazabicyclo(2.2.2)octane, also known as triethylenediamine, is a symmetrical, high melting (m.p. 159.8° C.) compound. The introduction of methyl groups into the triethylenediamine structure destroys its symmetry and results in liquid homologs of triethylenediamine. 2-Methyltriethylenediamine is a racemic mixture of two optically active isomers. Oxidation of triethylenediamine by hydrogen peroxide gives a mono- and a dioxide, while 2-methyltriethylenediamine yields two monoxides and a dioxide. These *N*-oxides can be identified by their characteristic NMR spectra. Quaternary salts of triethylenediamine and monoquaternary salts of methyltriethylenediamine form readily because of the freedom from hindrance at the nitrogens. The same property permits facile formation of addition compounds with one and two moles of bromine and iodine. These complexes are very stable insoluble compounds of the charge-transfer type and also form with the mono-*N*-oxide and monoquaternary salts of triethylenediamine.

Table I. Properties of Triethylenediamine and 2-Methyltriethylenediamine

	Triethylenediamine	Methyltriethylenediamine
Molecular weight	112.17	126.196
Appearance	Hygroscopic, white crystals	Slightly viscous liquid
Odor	Ammoniacal	Ammoniacal
Melting point, ° C.	159.8	Indefinite, glass at −70
Boiling point, ° C.	174	184
Refractive index, n_D^{26}		1.4789
Basicity, pK_{A1}	2.95	3.15
pK_{A2}	8.60	8.86
p-Nitrophenolate, m.p., ° C.	182-3	102-4

I. The most striking difference between the two compounds is the wide liquid range of 2-methyltriethylenediamine covering more than 200° C. (from below zero to 184° C.) compared with less than 15° C. for the liquid range of triethylenediamine.

Partial resolution of the optical isomers of 2-methyltriethylenediamine was affected from the salt formed with *d*-tartaric acid. The crystallized salt fraction yielded, after neutralization and separation of the free amine, a product with a specific rotation of +69.11, while the liquid fraction gave a product with a rotation of −29.49°. Evidently, the liquid fraction still contained an appreciable portion of the unresolved racemic mixture.

The infrared spectra of triethylenediamine (in CCl_4 and CS_2 solution) and its methyl derivative (neat) are compared in Figure 1. The two spectra are very similar, the main difference being the presence of a C-methyl band at 1380 cm.$^{-1}$ in the spectrum of 2-methyltriethylenediamine.

Since all the protons in triethylenediamine are equivalent, its NMR spectrum consists of a single symmetrical peak (2.72 p.p.m.) in D_2O. The NMR spectrum of the methyl derivative in D_2O shows two groups of peaks, a doublet at 1.11 (J = 6 c.p.s.) and a complex pattern with an intense peak at 2.73 p.p.m. The peaks at 1.11 p.p.m. are due to the methyl group and appear as a doublet because of the spin-spin coupling with the hydrogen on the ring carbon that bears the methyl group. The ring protons yield a complex pattern because of their nonequivalence (owing to the substituting methyl) which now allows them to undergo spin-spin coupling.

N-OXIDES OF TRIETHYLENEDIAMINE

The mono- and di-*N*-oxides of triethylenediamine have

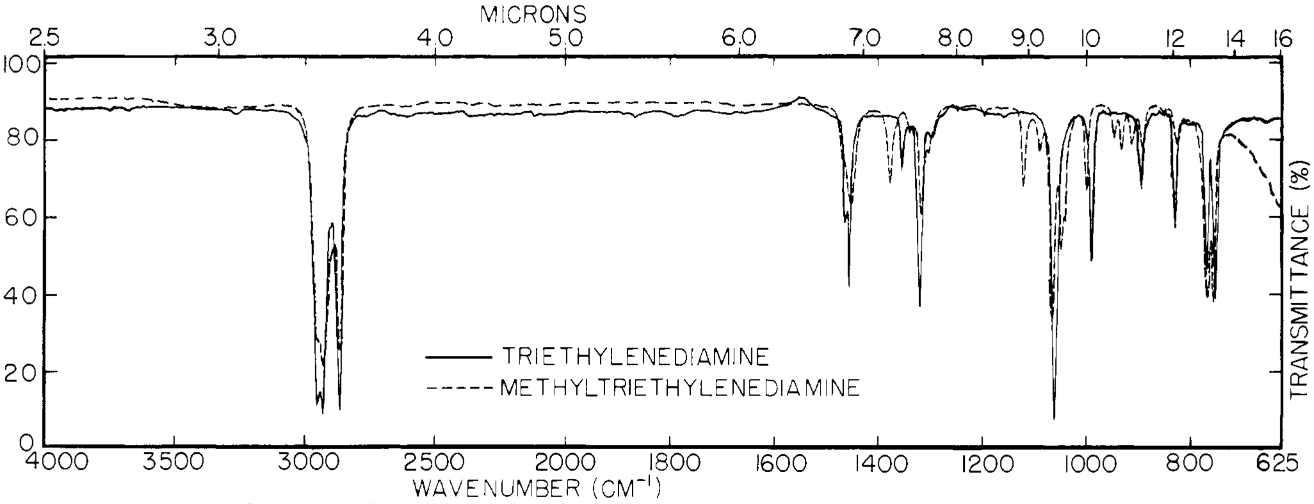


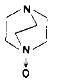
Figure 1. Infrared spectrum of triethylenediamine and methyltriethylenediamine

— Triethylenediamine. Cell thickness 0.1 mm. 25% in CCl_4 to 800 cm.$^{-1}$, 25% in CS_2 for 800–625 cm.$^{-1}$

---- Methyltriethylenediamine. Neat between salt plates been prepared earlier in these laboratories (*4*). In benzene solvent, molar amounts of hydrogen peroxide will precipitate the mono-*N*-oxide. Additional hydrogen peroxide and longer reaction times are necessary for the formation of the *N,N'*-dioxide. Both the *N*-oxide and the *N,N'*-dioxide are extremely hygroscopic solids; therefore, it is most difficult to isolate an anhydrous material even after rigorous drying of the products. Oswald and Guertin (*23*) and Heydkamp (*11*) encountered this problem in their synthetic work and have reported the products as the hydrates.

Elemental analysis of the *N*-oxides is not sufficiently reliable to distinguish between retained water and *N*-oxide oxygen; however, NMR analysis of the *N*-oxides in various solvents allows this distinction to be made.

The NMR spectrum of triethylenediamine mono-*N*-oxide in D_2O shows up as a singlet at 3.25 p.p.m. and not as the expected A_2B_2 pattern. The strong association with water evidently makes all the protons magnetically equivalent. In pyridine solution, however, a complex A_2B_2 pattern does appear at 3.15 p.p.m. demonstrating the nonequivalence of the ring protons and thus confirming the mono-*N*-oxide structure (I).



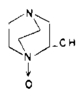
(I)

It is interesting to note the deshielding of the protons in the *N*-oxide relative to the parent compound (3.25 as compared with 2.72 p.p.m.), which apparently reflects the inductive effect of the quaternary nitrogen. The NMR spectrum of triethylenediamine di-*N*-oxide showed an even greater deshielding with the proton resonances appearing at 4.0 p.p.m. in D_2O.

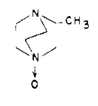
Introduction of the oxygen also reduces the basicity of triethylenediamine. A pK_a value of 4.07 was determined for the mono-*N*-oxide by titration in aqueous solution. The di-*N*-oxide was too weak a base to be titrated.

N-OXIDES OF METHYLTRIETHYLENEDIAMINE

The *N*-oxides of methyltriethylenediamine were prepared by the reaction of methyltriethylenediamine and 30% hydrogen peroxide. In this case, the presence of the methyl group on the ring gives rise to the possibility of two isomers of the mono-*N*-oxide, (II) and (III).



(II)



(III)

The monoxide was obtained as a solid. Its NMR spectrum in D_2O showed two methyl doublets, one at 1.23 p.p.m. (J = 6 c.p.s.) and the other at 1.36 p.p.m. (J = 6 c.p.s.) indicating it to be a mixture of (II) and (III). In isomer (II) (2-methyl-4-aza-1-azoniabicyclo[2.2.2]octane-1-oxide), the methyl group is closer to the *N*-oxide and hence its deshielding should be greater than the methyl in isomer (III) (3-methyl-4-aza-1-azoniabicyclo[2.2.2]octane-1-oxide) in which the methyl group is farther removed from the oxygen. Therefore, the methyl doublet of isomer (II) should appear at lower field (1.36 p.p.m.) than that of isomer (III) (1.23 p.p.m.). The chemical shift of the ring protons of the mixture comes at a lower field (3.28 p.p.m.) than for those in 2-methyltriethylenediamine (2.73 p.p.m.).

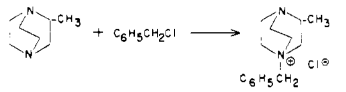
When pyridine was used as solvent, the two methyl doublets had chemical shifts of 1.5 and 1.12 p.p.m. for the (II) and (III) isomer, respectively, with no overlap between the two sets of peaks. Integration of this spectrum showed that the *N*-oxide mixture contained 33% isomer (II) and 67% isomer (III), indicating a preferential attack of the sterically less hindered nitrogen in the four position by hydrogen peroxide.

Figure 2 shows the methyl peaks of the solid product obtained when the mixture of the mono-*N*-oxides (II) and (III) is treated with hydrogen peroxide. The methyl doublets result from the presence of the *N*-oxide (III) (1.23 p.p.m.) and the di-*N*-oxide (IV) (1.5 p.p.m., J = 6 c.p.s.). A small amount of isomer (II) is present as indicated by the weak absorption at 1.36 p.p.m. and the reversed intensities of the methyl doublet at 1.5 p.p.m. The authors, therefore, conclude that isomer (II), once formed, is more readily oxidized than isomer (III) which further demonstrates the steric blocking effect of the methyl group. The ring protons of 2-methyltriethylenediamine di-*N*-oxide appear as a complex pattern centering at 3.95 p.p.m. The pK_a value for the methyltriethylenediamine mono-*N*-oxide mixture was 4.18, but again, the di-*N*-oxide could not be titrated.

QUATERNARY COMPOUNDS OF TRIETHYLENEDIAMINE AND METHYLTRIETHYLENEDIAMINE

Triethylenediamine forms quaternary salts even in a nonpolar solvent such as benzene (*11*) when allowed to react with an alkyl or aralkyl halide. In benzene solution, the monoquaternary salts are formed selectively because the monoquaternary salt is insoluble in benzene and crystallizes out of the solution. This, thus, avoids reaction with a second mole of the alkyl halide.

The preferential formation of the monoquaternary salt in benzene obtains also in the quaternization of methyltriethylenediamine. In this case, however, the diquaternary salts are difficult to form even in a polar solvent apparently because of steric hindrance at the nitrogen in the one position. In the preparation of the monoquaternary salt from methyltriethylenediamine and benzyl chloride, the authors observed that the nitrogen in the four position was preferentially attacked.



The NMR spectrum of this compound in D_2O shows the methyl protons at 1.27 p.p.m., close to the value obtained for the methyl protons of 1,3-dimethyl-4-aza-1-azoniabicyclo(2.2.2)octane oxide [isomer (III)].

The findings were similar in the preparation of the monomethyl iodide salt of methyltriethylenediamine. This monoquaternary salt forms even at room temperature in almost

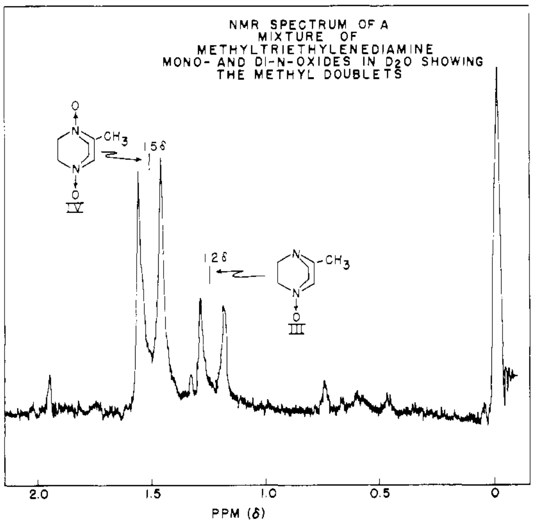


Figure 2. NMR spectrum of a mixture of methyltriethylenediamine mono- and di-*N*-oxides in D_2O showing the methyl doublets

quantitative yield in benzene solution. The NMR spectrum shows the methyl doublet at 1.24 p.p.m. (J = 6 c.p.s.) and only a very small broad absorption around 1.36 p.p.m. Apparently, the 3-methyl isomer forms almost exclusively.

The diquaternary salt did not form when a molar excess of methyl iodide was reacted with methyltriethylenediamine in benzene, and only the monomethiodide was isolated. Even in ethanol an excess of methyl iodide and methyltriethylenediamine produced only the monoquaternary salt. The diquaternary salt was obtained in low yield only after heating the monoquaternary salt with excess methyl iodide in ethanol for 30 minutes.

The dimethiodide salt of methyltriethylenediamine in D_2O exhibits a very interesting NMR spectrum (Figure 3). The N-methyl peaks appear as two distinct singlets at 3.4 and 3.3 p.p.m. This shows that the two N-methyl groups are not equivalent because of the influence of the C-methyl substituent. Furthermore, the C-methyl group appears as a complex set of peaks at 1.61 p.p.m. and not as the expected doublet. This is due probably to long range spin-spin coupling with the ring methylene protons.

ADDITION COMPOUNDS OF TRIETHYLENEDIAMINE AND METHYLTRIETHYLENEDIAMINE WITH BROMINE AND IODINE

The preparation of the 1 to 2 addition compounds of triethylenediamine with bromine and iodine has been accomplished earlier in these laboratories (*10*). These compounds form readily in organic solvents and are high melting, insoluble solids which decompose in the presence of acids. The bromine addition compounds form, also, from an aqueous solution in essentially quantitative yield, so that this reaction could be used for the analytical determination of triethylenediamine in an aqueous solution.

The extreme stability of these adducts and the ease of their preparation has prompted the authors to investigate the nature of these compounds and to prepare similar addition compounds with 2-methyltriethylenediamine and with some other triethylenediamine derivatives.

In the following discussion, the authors shall designate as the monobromo or monoiodo adduct the addition compounds containing 1 mole of halogen per mole of diamine and as the diadduct the addition compound containing 2 moles of halogen per mole of diamine.

NATURE OF THE TRIETHYLENEDIAMINE-IODINE ADDUCT

Nagakura (*21*) showed that in the iodine complex of triethylamine the bonding depends on the formation of a charge transfer complex which shows a characteristic absorption band in the near ultraviolet at 278 mμ. Spectroscopic measurements carried out in the system triethylenediamine-iodine in n-heptane solution at room temperature showed an absorption band appearing at 311 mμ indicating the formation of a charge transfer complex also in this case. Figure 4 shows the spectrum of a solution containing iodine and triethylenediamine, together with the spectra of solutions of iodine and triethylenediamine.

To determine the equilibrium constant for the adduct formation defined by:

$$K = [(\text{complex})/(\text{amine})\ (\text{iodine})]$$

measurements were made of the absorbance of the complex at 25° C. at various iodine and triethylenediamine concentrations. The results (Table II) were treated according to the method of Benesi and Hildebrand (*1*) by plotting iodine concentration-absorbance *vs.* the reciprocal amine concentration. For a 1 to 1 complex, this plot is expected to have a straight line portion for high amine concentrations. The intercept on the ordinate is then equal to the reciprocal value of the extinction coefficient (ϵ), while the slope of the straight line portion is equal to the reciprocal value of the product $K\epsilon$. Figure 5 shows this type of plot. Because of a reaction between the iodine and the solvent and equipment limitations, spectroscopic measurements were not sufficiently reproducible and accurate to define the straight line portion of the plot and thus to allow an exact determination of the equilibrium constant. The curve shown on the figure was calculated for an equilibrium constant $K = 10^5$ and $\epsilon = 5.5 \times 10^3$ and appears to be in reasonably good agreement with the experimental points. This equilibrium constant is thought to be reliable within ± 20% and is at least 10 times as large as the corresponding equilibrium constant measured for the iodine-triethylamine system (*21*) (4.68×10^3).

MISCELLANEOUS HALOGEN COMPLEXES OF TRIETHYLENEDIAMINE AND METHYLTRIETHYLENEDIAMINE

In addition to the mentioned dibromo-diiodo complexes of triethylenediamine, the authors have also prepared related adducts using triethylenediamine and methyltriethylenediamine. The 1 to 1 triethylenediamine-bromine compound was prepared from bromine and excess amine. The product precipitated from the solution as a yellow solid in 98% yield. Its properties are similar to the tetrabromo derivative.

The mono- and dibromo adducts of methyltriethylenediamine were similarly prepared in 90 and 98% yields,

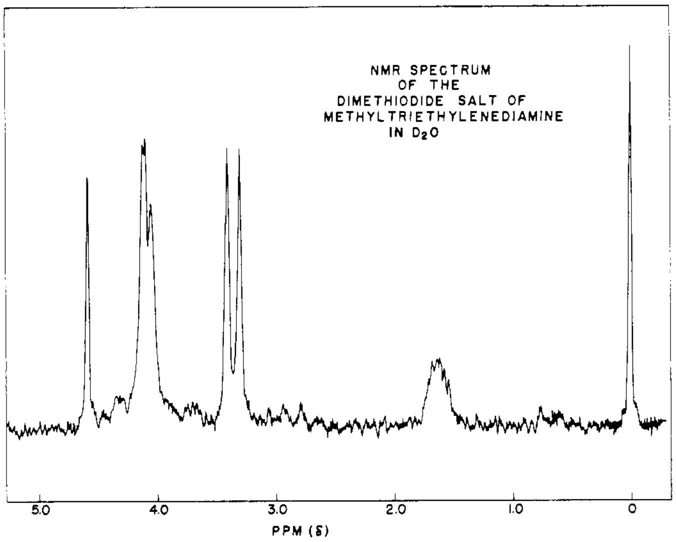


Figure 3. NMR spectrum of the dimethiodide salt of methyltriethylenediamine in D_2O

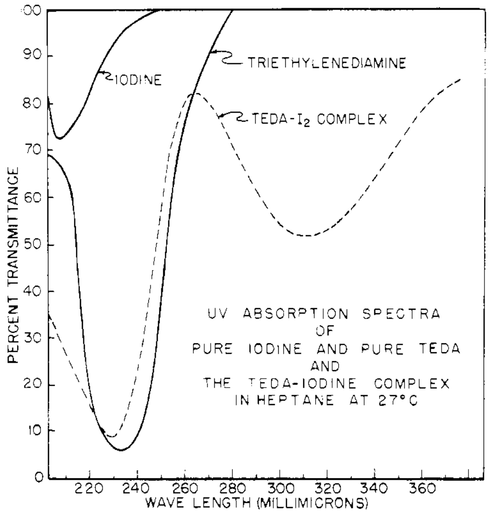


Figure 4. Ultraviolet absorption spectra of pure iodine and the TEDA-iodine complex in heptane at 27° C.

Table II. Absorbance of Triethylenediamine-Iodine Charge-Transfer Complex (CT) at 311 Millimicrons in Heptane at 27° C.

Initial Concentration of Iodine $[I_2]$, Moles/Liter x 10^5	Initial Concentration of Triethylenediamine, $[D]$ Moles/Liter, x 10^5	Absorbance of CT Band at 311 Mμ	$[I_2]$/Absorbance x 10^{-4}
6	28.0	0.287	2.09
6	20.0	0.318	1.88
6	18.0	0.322	1.86
6	16.0	0.310	1.93
6	14.0	0.302	1.98
4	14.0	0.177	2.26
6	12.0	0.295	2.04
6	10.0	0.275	2.18
4	10.0	0.168	2.38
6	8.0	0.265	2.26
4	8.0	0.161	2.48
4	6.0	0.147	2.72
4	5.2	0.142	2.82
4	4.8	0.130	3.08
4	4.0	0.098	4.08

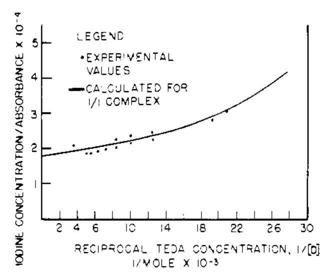


Figure 5. Relationship between $[I_2]$/absorbance and $1/[D]$ at 27° C. λ_{max} = 311 mμ

respectively. Again, the properties of these compounds were similar to the corresponding triethylenediamine complexes; however, they were more soluble in organic solvents such as acetone, benzene, dimethylformamide, and dimethyl sulfoxide.

The diiodo complex of methyltriethylenediamine was obtained in good yield by the reaction of excess iodine with the amine. Attempts to prepare the monoiodo adduct using methyltriethylenediamine, however, produced only the diiodo complex.

The monobromo adduct of a quaternary salt of triethylenediamine was prepared by the reaction of 1-benzyl-4-aza-1-azoniabicyclo(2.2.2)octane chloride with bromine in an aqueous solution. Halogen analysis indicated that the compound had the following structure:

$$(C_6H_5CH_2\overset{+}{N}[C_2H_4]_3N\cdot Br_2)Cl$$

In a similar manner, excess bromine was reacted with triethylenediamine mono-*N*-oxide to form a yellow precipitate which appears to be the dibromo adduct of triethylenediamine mono-*N*-oxide.

$$O \leftarrow N(C_2H_4)_3N\cdot 2Br_2$$

EXPERIMENTAL

Equilibrium Constant for the Formation of the Triethylenediamine-Iodine Charge-Transfer Adduct. Measurement of the equilibrium constant was made using essentially the same technique described by Nagakura (*21*). The ultraviolet spectra were obtained on a Bausch and Lomb 505 spectrophotometer with a 1-cm. light path quartz cell. The solvent, *n*-heptane, was purified by distillation and stored over calcium chloride under a nitrogen atmosphere.

To minimize the effect of light upon the stability of the solution, the samples were made up immediately prior to use in dark volumetric flasks. The ultraviolet spectrum was scanned immediately after the solutions were made up. To avoid precipitation of the adduct, very dilute concentrations in the order of $10^{-5}M$ iodine and 10^{-4} to $10^{-5}M$ triethylenediamine were employed.

NMR and IR Spectral Measurements. The Varian A60A NMR spectrometer was used to obtain the spectra. When deuterium oxide was used as solvent, 3-(trimethylsilyl)-1-propanesulfuric acid (Tiers salt) was used as the reference, while in all other solvents, tetramethylsilane was used. Chemical shifts are reported in parts per million (p.p.m.) below the reference compound. Solution concentrations were in the order of 15 to 20%. Infrared measurements were obtained on a Perkin-Elmer 237 Infracord spectrometer.

2-Methyltriethylenediamine. This compound was prepared according to the procedure described by Farkas, Hersh, and Mascioli (*5, 6*).

Separation of the Optical Isomers of Methyltriethylenediamine. Methyltriethyleneidamine (52.0 grams, 0.41 mole) was dissolved in 100 ml. of methanol. Tartaric acid (*d*-form) (63 grams, 0.42 mole) was dissolved in 250 ml. of methanol and added dropwise with stirring to the amine. A white solid precipitated and after filtration, washing with methanol, followed by drying, 49 grams of solid were recovered. After removal of the solvent from the filtrate, 74 grams of a viscous liquid were obtained. The amine was recovered from the acid salt by neutralization with excess 50% NaOH solution and extraction with toluene. The fractions were separated using a gas chromatographic prep column containing alkaline UCON on Chromosorb. The purified materials had specific rotations of 69.11° and −29.49°.

1,4-Diazabicyclo(2.2.2)Octane *N*-Oxide. To a solution of 112 grams (1 mole) of triethylenediamine in 500 ml. of benzene was added rapidly 113 grams (1 mole) of H_2O_2 (30%) with stirring at room temperature. A precipitate formed at once. Water was removed from the reaction mixture by means of a Dean-Stark apparatus. The solids were filtered off and washed with three 100-ml. portions of ether. After drying in a vacuum oven at 40° C. for 24 hours, 90 grams (61.5%) of product were recovered, m.p. 121–3° C. Anal. Calcd. for $C_6H_{12}N_2O\cdot 0.5\ H_2O$: C, 52.50; H, 9.48; N, 20.44; Found: C, 51.80; H, 9.69; N, 20.28.

1,4-Diazabicyclooctane 1,4-*N,N'*-Dioxide. Triethylenediamine was dissolved in water (22.4 grams, 0.2 mole, in 100 ml.). Hydrogen peroxide, 60 grams, 30% H_2O_2 (0.53 mole), was added slowly with stirring. After heating slowly to 70° C. then cooling to room temperature, 300 ml. of benzene were added, and the excess water was removed by azeotropic distillation. The recovered product contained approximately 22% of the mono-*N*-oxide. To complete the reaction, the procedure was repeated adding an additional 20.8 grams of H_2O_2 (30%). The product was recovered, washed with pentane, and dried in the vacuum oven at 40° C. The recovered solid, 29.0 grams (85% theory), had a m.p. >300° C. Anal. calcd. for $C_6H_{12}N_2O_2\cdot 1.5\ H_2O$: C,

Table III. Halogen Complexes of Triethylenediamine, Methyltriethylenediamine and Some of Their Derivatives

Compound	Solvent	Yield, %	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found	Halogen Calcd.	Halogen Found
Triethylenediamine $\cdot Br_2$	Benzene	99	26.49	27.18	4.45	4.62	10.30	10.76	58.76	59.7
1-Benzyl-4-aza-1-azoniabicyclo(2.2.2)octane chloride $\cdot Br_2$	Water	78							48.99	49.9
Triethylenediamine *N*-oxide $\cdot 2Br_2$	Water		16.09	16.35	2.69	3.18	6.27	6.14	71.39	71.0
Methyltriethylenediamine $\cdot 2Br_2$	Benzene	98	18.86	19.28	3.17	3.22	6.28	6.09	71.69	71.70
Methyltriethylenediamine $\cdot 2I_2$	Ethanol	69.6	13.26	13.68	2.23	2.01	4.42	4.40	80.09	79.1

42.25; H, 8.83; N, 16.38; Found: C, 41.76; H, 8.87; N, 16.08.

2-Methyl-1,4-Diazabicyclo(2.2.2)Octane *N*-Oxide. To a solution of 47.0 grams (0.383 mole) of 2-methyltriethylenediamine in 250 ml. of cyclohexane were added with stirring 47.5 grams (0.42 mole) of H_2O_2 (30%). The water layer was removed by azeotropic distillation using a Dean-Stark trap. The cyclohexane solvent and excess reactants were stripped off under vacuum. The residual material was washed with 200 ml. of pentane. After drying in a vacuum oven at 35° C., 22 grams of a tan solid were recovered, 36% yield, m.p. 55° to 65° C. Anal. calcd. for $C_7H_{14}N_2O\cdot H_2O$: C, 52.50; H, 10.01; N, 17.50; Found: C, 52.93; H, 10.52; N, 17.10. NMR analysis of this product showed that the 2-methyl-4-*N*-oxide isomer was present in 65.3% while the 2-methyl-1-*N*-oxide isomer concentration was 34.7%.

2-Methyl-1,4-Diazabicyclooctane 1,4-*N,N'*-Dioxide. To a solution of 25 grams (0.198 mole) of methyltriethylenediamine in 100 ml. water were added dropwise 60 grams (0.53 mole) of H_2O_2 (30%). Reaction temperature was slowly raised to 70° C. After the solution cooled, 300 ml. of benzene were added, and the excess water was removed by azeotropic distillation. Recovery of the product and analysis by NMR showed 78% dioxide and 22% monoxide. The procedure was repeated by adding 19.2 grams of H_2O_2 (30%). After workup and drying of the product, 34.2 grams of solid (85.2% theory) were recovered. The hydrate had a melting point of 201-6° C. Anal. calcd. for $C_7H_{14}N_2O_2\cdot 2.5\ H_2O$: C, 41.40; H, 9.37; N, 13.81; Found: C, 41.46; H, 9.89; N, 13.99.

1-Benzyl-3-Methyl-4-Aza-1-Azoniabicyclo(2.2.2)Octane Chloride. To a benzene solution of 54 grams (0.42 mole) of methyltriethylenediamine were added a solution of 50 grams (0.40 mole) of benzyl chloride in 300 ml. of benzene. The mixture was stirred well at room temperature. After the mixture stood overnight, the solids were filtered, washed with pentane, and dried in a vacuum oven. Yield: 70 grams (70%) of a white solid, m.p. 194-6° C. Anal. calcd. for $C_{14}H_{21}ClN_2$: C, 66.40; H, 8.32; N, 10.69; Found: C, 66.46; H, 8.56; N, 11.04.

1,3-Dimethyl-4-Aza-1-Azoniabicyclo(2.2.2)Octane Iodide. To 1.3 grams of methyltriethylenediamine in 50 cc. of benzene there were added 1.4 grams of methyl iodide. The white precipitate which formed was removed by filtration, washed with hexane, and dried in a vacuum oven. Purification was accomplished by recrystallizing the crude material from 95% ethanol. Yield: 2.6 grams (98%). The NMR spectrum of this material obtained in D_2O is discussed in the text. Anal. calcd. for $C_8H_{17}IN_2$: C, 35.83; H, 6.39; N, 10.45; I, 47.33; Found: C, 35.6; H, 6.81; N, 10.72; I, 47.8. When an excess of methyl iodide was added to methyltriethylenediamine, only the monoquaternary salt was isolated.

1,2,4-Trimethyl-1,4-Diazoniabicyclo(2.2.2)Octane Diiodide. To 3.5 grams of 1,3-dimethyl-4-aza-1-azoniabicyclo(2.2.2)-octane iodide in 100 cc. of ethanol were added 5 grams of methyl iodide. After heating for one-half hour on a steam bath, the solution was cooled to room temperature. A white precipitate was removed by filtration. After washing with fresh ethanol, the material was dried in a vacuum oven. Yield: 0.5 grams (9% of theoretical). The NMR spectrum of the compound was obtained in D_2O. See text for the description of the spectrum. Anal. calcd. for $C_9H_{20}I_2N_2$: C, 26.36; H, 4.92; N, 6.83; I, 61.91; Found: C, 25.93; H, 5.08; N, 7.08; I, 61.7.

Triethylenediamine Monobromo Adduct. To a solution of 6.0 grams of triethylenediamine in 100 ml. of benzene were added 8 grams of bromine. A yellow precipitate formed instantly. This solid was removed by filtration and washed six times with benzene to remove excess triethylenediamine. It was then washed with hexane and dried in a vacuum oven at 50° C. Yield: 13.5 grams (99%). (For elementary analysis see Table III.)

Other Bromo and Iodo Adducts. Various other mono- and dibromo and iodo adducts of triethylenediamine, of its methyl homolog, *N*-oxide, and monoquaternary salt were prepared by analogous procedures. The solvents used and yields obtained in each case are summarized in Table III, which also shows the experimental and calculated elementary analysis.

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LITERATURE CITED

(1) Benesi, H. A., Hildebrand, J. H., *J. Am. Chem. Soc.* **71**, 2703 (1949).
(2) Farkas, A. (to Air Products & Chemicals, Inc.), U.S. Patent **2,950,282** (Aug. 23, 1960).
(3) Farkas, A., Flynn, K. G., *J. Am. Chem. Soc.* **82**, 642 (1960).
(4) Farkas, A., Herrick, E. C. (to Air Products & Chemicals, Inc.), U.S. Patent **3,038,903** (June 12, 1962).
(5) Farkas, A., Hersh, J. M., Mascioli, R. L. (to Air Products & Chemicals, Inc.), U.S. Patent **3,167,518** (Jan. 26, 1965).
(6) *Ibid.*, U.S. Patent **3,167,555** (Jan. 26, 1965).
(7) Farkas, A., Krause, J. H. (to Air Products & Chemicals, Inc.), U.S. Patent **2,977,363** (March 28, 1961).
(8) Farkas, A., Oakes, M. D. (to Air Products & Chemicals, Inc.), U.S. Patent **3,123,607** (March 3, 1964).
(9) Herrick, E. C. (to Air Products & Chemicals, Inc.), U.S. Patent **2,937,176** (May 17, 1960).
(10) *Ibid.*, U.S. Patent **2,964,526** (Dec. 13, 1960).
(11) Heydkamp, W., Ph.D. thesis, University of Munich, Munich, Germany, 1961.
(12) Houdry Process & Chemical Co., Division of Air Products & Chemicals, Inc., Technical Bulletin, "DABCO Cocatalyst System for One-Shot Rigid Urethane Foam," 1964.

(13) *Ibid.*, "DABCO Triethylenediamine (1,4-Diazabicyclo(2.2.2)-Octane, Properties, Reactions and Applications," 1965.
(14) *Ibid.*, "Cocatalyst System with DABCO for Soft to Firm Flexible Slabstock Foams," 1961.
(15) *Ibid.*, "Triethylenediamine (DABCO) Urethane Catalyst," 1960.
(16) Hromatka, O., *Ber.* **75B**, 1302 (1942).
(17) Krause, J. H. (to Air Products & Chemicals, Inc.), U. S. Patent **2,985,658** (May 23, 1961).
(18) Mascioli, R. L. (to Air Products & Chemicals, Inc.), U. S. Patent **3,166,558** (Jan. 9, 1965).
(19) Miller, F. (to Air Products & Chemicals, Inc.), U. S. Patent **3,150,138** (Sept. 22, 1964).
(20) *Ibid.*, U. S. Patent **3,213,096** (Oct. 19, 1965).
(21) Nagakura, S., *J. Am. Chem. Soc.* **80**, 520 (1958).
(22) Orchin, M. (to Air Products & Chemicals, Inc.), U. S. Patent **2,939,851** (June 7, 1960).
(23) Oswald, A.A., Guertin, D.L., *J. Org. Chem.* **28**, 651 (1963).

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Substitutive Chlorination of Naphthalene Esters

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Naphthalene esters are easily chlorinated by molecular chlorine in chlorinated organic solvents in the presence of small amounts of ferric chloride. This method is a convenient synthesis of highly chlorine-substituted naphthalene acids and esters which heretofore have been difficult to prepare.

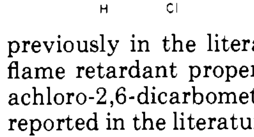
THE DIRECT CHLORINATION of aromatic acids, including naphthalenecarboxylic acids, is difficult. Naphthalene carboxylate esters are easily chlorinated by molecular chlorine in the presence of small amounts of ferric chloride, and this is the easiest method for synthesizing chlorinated naphthalenecarboxylic acids and their derivatives.

To substitute three or more chlorines on the rings of naphthalenecarboxylic acids requires rather drastic conditions. By using concentrated sulfuric acid as solvent, 1,8-naphthalic anhydride has been chlorinated in good yield to tetrachloro-1,8-naphthalic anhydride in the presence of ferric sulfate (*3*). On the other hand, alkylaromatic hydrocarbons readily undergo nuclear chlorination under much milder conditions. They are generally reacted with molecular chlorine in a chlorinated organic solvent, such as carbon tetrachloride, in the presence of various catalysts, such as metallic salts, pyridine, and iodine (*1, 5, 6, 7, 10, 11*). Under these latter conditions, naphthalenecarboxylic acids are not chlorinated, but the methyl esters undergo ready nuclear chlorination using similar conditions.

Compounds with ester groups on both rings, such as 2,6-dicarbomethoxynaphthalene, as well as compounds with an ester group on only one ring, such as α- and β-methyl naphthoates, can be chlorinated by this method. The ester is dissolved in a chlorinated organic solvent, such as carbon tetrachloride, tetrachloroethylene or 1,1,2,2-tetrachloroethane, containing ferric chloride and iron and the solution is treated with molecular chlorine. The extent of chlorine substitution depends on several factors, including solvent and time and temperature of reaction. It becomes increasingly difficult to substitute chlorines on the rings when a number of positions are occupied, though most difficulty is encountered in substituting the last available position. Low boiling solvents, such as carbon tetrachloride, have poor solubility properties for the esters and the extent of chlorine substitution is low. Tetrachloroethylene is a good solvent for the reaction, but is not inert to chlorine under the conditions used and long reaction times are necessary for extensive substitution. By using 1,1,2,2-tetrachloroethane as solvent, highly substituted materials can be obtained in a short reaction time with efficient use of chlorine. The product is worked up by steam distillation to remove solvent and the water insoluble product collected and purified by either distillation or crystallization from solution.

Unless complete substitution was achieved, mixtures of chlorinated products were obtained in most experiments. Starting material was not recovered in any experiments, so that crude yields were high. Results for typical experiments are given in Table I. The products were identified by infrared and nuclear magnetic resonance (NMR) spectroscopy and by elemental analyses.

No study was made of the position of the chlorines on chlorinated α- and β-methyl naphthoates. They are probably mixtures. NMR spectroscopy gave good evidence for the structure of the tetrachloro-2,6-dicarbomethoxynaphthalene. This material was the easily crystallized material from a gross reaction mixture. The remainder of the product was an oily material that could not be induced to crystallize. Since it had the same number of aromatic hydrogens (two) as the easily crystallized compound, it was assumed to be a mixture of isomeric tetrachloro-2,6-dicarbomethyoxynaphthalenes. The NMR spectrum of the crystallized tetrachloro compound showed that the ester groups were in similar environments and that the hydrogens were different and not coupled. There are nine possible tetrachloro isomers. Three were ruled out because they have equivalent hydrogens and five more were ruled out because the ester groups were in different environments, one being flanked by two chlorines and the other flanked by either one or no chlorines. Therefore, it was concluded that the material was 1,4,7,8-tetrachloro-2,6-dicarbomethoxynaphthalene (I). This compound has not been reported previously in the literature. It has been found to render flame retardant properties to reinforced plastics (*2*). Hexachloro-2,6-dicarbomethoxynaphthalene also has not been reported in the literature.



H TYPE	CHEMICAL SHIFT
-COOCH$_3$	4.02 ppm
AROMATIC	7.67 ppm 8.50 ppm

I

Under prolonged chlorination conditions, the naphthalene esters are degraded to chlorocarbon compounds. Octachloronaphthalene, 1,4-dihydronaphthalene (isolated as the quinone) and decachloroindan have been isolated from the

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