error of the measurements.[15] The quadrupole splitting ($\Delta E = 1.53 \pm 0.04$ mm sec^{-1}, independent of temperature from room temperature down to liquid nitrogen temperature) corresponds to an orbital doublet ground state,[16] while the chemical shift (δ +1.16 ± 0.04 mm sec^{-1} at room temperature, relative to an iron foil absorber) is characteristic of high-spin iron(II) complexes. The orbital doublet ground state implies that both forms possess a fairly high degree of geometrical and orbital symmetry. Such a ground state can be realized by any one of several arrangements of pyridine rings in the *trans* isomer but by only one, rather unlikely, arrangement of pyridine rings in a *cis* isomer.

The X-ray patterns of single crystals of the two forms were also found to be identical with regard to both spot positions and relative intensities.[15,17] The cell dimensions of the two forms are $a = 12.38 \pm 0.02$ A, $b = 13.04 \pm 0.02$ A, $c = 16.42 \pm 0.02$ A, and $\beta = 118.1 \pm 0.1$. Moreover, the crystals are isomorphous with $Ni(py)_4(NCS)_2$ and $Co(py)_4(NCS)_2$, whose structures have been determined by Porai-Koshits and Antsishkina.[18] In these compounds the thiocyanate groups are *trans* to each other and the nitrogen end of the thiocyanate is attached to the metal. The similarity of the X-ray spectra of the yellow and violet forms together with the fact that the crystals are isomorphous with $Ni(py)_4(NCS)_2$ and $Co(py)_4(NCS)_2$ establishes that both forms have a *trans* structure and rules out the possibility of linkage isomerism.

We conclude, therefore, that the yellow form (λ_{max} ~365 mμ in chloroform) has a *trans*-octahedral configuration[19] and is not the *cis* isomer as claimed by Spacu, *et al.*,[9] and that the violet form (λ_{max} ~525 mμ in chloroform[20]) is essentially an impure version of the yellow form, the impurity being traces of iron(III).

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(15) The Mössbauer and X-ray measurements were not sufficiently sensitive to detect the small amount of iron(III) (0.40%) present in the violet form.

(16) G. R. Hoy and F. de S. Barros, *Phys. Rev.*, **139A**, 929 (1965).

(17) These measurements were performed by Dr. Elmer O. Schlemper at the Chemistry Department, Brookhaven National Laboratory, Upton, N. Y.

(18) M. A. Porai-Koshits and A. S. Antsishkina, *Soviet Phys.-Cryst.*, **3**, 694 (1958).

(19) Goodgame, *et al.*,[2] have also proposed that (yellow) $Fe(py)_4(NCS)_2$ has a *trans*-octahedral structure on the basis of the similarity of the X-ray powder photographs of $Fe(py)_4(NCS)_2$ and $Ni(py)_4(NCS)_2$.

(20) The peak at 525 mμ in the spectrum of the violet form is present in addition to the peak at 365 mμ, which is also found in the spectrum of the yellow form.

CHEMISTRY DEPARTMENT
BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973

NILS E. ERICKSON
NORMAN SUTIN

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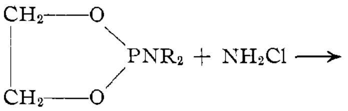
Triazanium ($NH_2NR_2NH_2^+$) Salts by Chloramination Reactions

Sir:

No unsubstituted hydronitrogen in the series N_nH_{2n+2} of higher molecular weight than N_2H_4 is known except for the possible formation of N_4H_6 (tetrazane) as a solid at −195°. According to Rice and Scherber[1] this material decomposes rapidly at −178° to nitrogen and ammonia. A very few substituted triazanes have been reported and none of these is a simple alkyl or aryl derivative, and in many instances the claimed triazane derivatives are of doubtful composition and not well-established identity. Recently, Gösl claimed the formation of a dialkyltriazanium salt[2] by the reaction of 1,1-dimethylhydrazine with hydroxylamino-O-sulfonic acid but gave no analytical data. Gösl indicated that studies of the infrared spectrum indicated that the dimethyltriazanium ion has the structure $[H_2NN(CH_3)_2NH_2]^+$, but no details were given to confirm this.

We wish to report the preparation of a series of new trizanium chlorides through the use of the chloramination reaction. Two procedures have been employed, apparently for the first time: (1) the treatment of a benzene solution of a 2-dialkylamino-1,3,2-dioxophospholane with a gaseous mixture of chloramine and excess ammonia, produced by the gas-phase chlorination of ammonia[3]



$$[H_2NNR_2NH_2]^+Cl^- + \text{unidentified products}$$

and (2) the treatment of a benzene solution of a 1,1-dialkylhydrazine with a gaseous mixture of ammonia and chloramine

$$R_2NNH_2 + NH_2Cl \longrightarrow [H_2NNR_2NH_2]^+Cl^-$$

Compounds prepared by the first procedure include the following.

2,2-Dimethyltriazanium Chloride.—The yield of purified product was 51%; mp 133.5–134.0° dec. *Anal.* Calcd for $C_2N_3H_{10}Cl$: C, 21.53; H, 9.03; N, 37.66; Cl, 31.77. Found: C, 21.20; H, 9.00; N, 37.78; Cl, 31.85.

2,2-Diethyltriazanium Chloride.—The yield of purified product was 62%; mp 135–136° dec. *Anal.* Calcd for $C_4N_3H_{14}Cl$: C, 34.41; H, 10.10; N, 30.09; Cl, 25.39. Found: C, 34.17; H, 10.21; N, 29.87; Cl, 25.39.

2,2-Cyclotetramethylenetriazanium Chloride.—The yield of purified product was 41%; mp 121–123° dec. *Anal.* Calcd for $C_4N_3H_{12}Cl$: C, 34.91; H, 8.79; N, 30.54; Cl, 26.04. Found: C, 33.08; H, 8.64; N, 29.55; Cl, 26.04. Though the carbon analysis is low, the remainder of the analytical data combined with the infrared and nmr data leave no doubt concerning the identity of this compound.

2,2-Dimethyltriazanium chloride was also prepared by the second procedure. The yield of purified product was 40%; mp 133–134° dec. *Anal.* Calcd for $C_2N_3H_{10}Cl$: C, 21.53: H, 9.03; N, 37.66; Cl, 31.77. Found: C, 21.34; H, 9.08; N, 37.54; Cl, 31.90.

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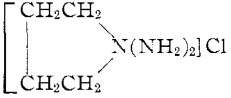
(1) F. O. Rice and F. Scherber, *J. Am. Chem. Soc.*, **77**, 291 (1955).

(2) R. Gösl, *Angew. Chem. Intern. Ed. Engl.*, **1**, 405 (1962).

(3) H. H. Sisler, F. Neth, R. Drago, and D. Yaney, *J. Am. Chem. Soc.*, **76**, 3906 (1954).

TABLE I

Compound	H^1 peaks (τ values)	Area ratios
$[(CH_3)_2N(NH_2)_2]Cl$	τ_{CH_3} 6.48, τ_{NH_2} 3.28	$H^1_{CH_3}:H^1_{NH_2} = 6:4$
$[(C_2H_5)_2N(NH_2)_2]Cl$	τ_{CH_3} 8.75, τ_{CH_2} 6.33, τ_{NH_2} 3.65	$H^1_{CH_3}:H^1_{CH_2}:H^1_{NH_2} = 5.9:4.1:3:9$
	$\tau_{CH_2'}$ 7.91, τ_{CH_2} 6.15, τ_{NH_2} 3.35	$H^1_{CH_2'}:H^1_{CH_2}:H^1_{NH_2} = 4:4:4$

Equimolar amounts of dimethyltriazanium chloride and silver nitrate were stirred in methanol for 10 min and the silver chloride filtered off. Addition of ether to the filtrate resulted in the precipitation of the triazanium nitrate. Recrystallization from an ethanol–ether mixture gave an 82% yield of a crystalline solid which decomposes at 125–126°. *Anal.* Calcd for $C_2H_{10}N_4O_3$: C, 17.39; H, 7.30; N, 40.56. Found: C, 17.50; H, 7.26; N, 40.54.

Four structures are possible for a disubstituted triazanium ion

$$\underset{\text{I}}{R_2N\overset{+}{N}H_2NH_2} \qquad \underset{\text{II}}{R_2NNH\overset{+}{N}H_3} \qquad \underset{\text{III}}{H_2N\overset{+}{N}R_2NH_2} \qquad \underset{\text{IV}}{\overset{+}{N}HR_2NHNH_2}$$

Examination of the H^1 magnetic resonance spectra of the triazanium chlorides prepared indicates strongly that structure III is the correct one in every case. Nmr data are summarized in Table I.

Strong bands at 3230, 3130, and 1620 cm^{-1} in the infrared spectrum of all three of the triazanium chlorides mentioned above may be assigned to NH_2 stretching and deformation vibrations and thus are in accordance with structure III.

Preliminary results indicate that $(CH_3)NNH(CH_3)$ and $(CH_3)_2NN{=}CH_2$ undergo chloramination to yield as a major product $[(CH_3)_2N(NH_2)_2]Cl$. This indicates that the N—N bond may be broken and then re-formed during the chloramination process. Studies of the range and the mechanism of these reactions are continuing.

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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF FLORIDA
GAINESVILLE, FLORIDA 32601

KURT UTVARY
HARRY H. SISLER

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