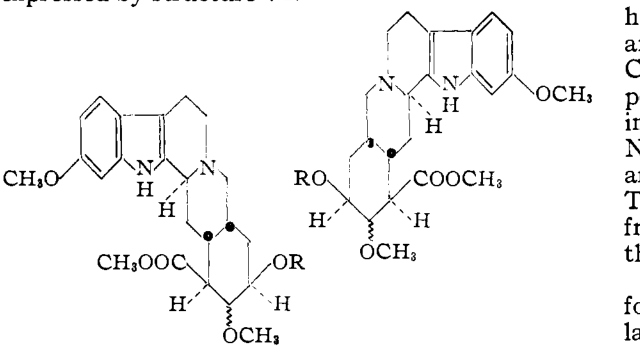
cis to the hydrogens at C-15 and C-20. In addition, the carbomethoxy group at C-16 is *cis* to the C-18 function since reserpic acid readily forms a γ-lactone without inversion.[1] Thus the known stereochemical relationships of reserpine can be expressed by structure VI.



VI VII

We have no conclusive evidence at present concerning the stereochemistry of the C-17 methoxyl group although, assuming a *trans* elimination in the formation of methyl anhydroreserpate, the 17-methoxyl would appear to be *cis* oriented.

It now seems possible to assign absolute configurations to the above mentioned asymmetric centers since Klyne has shown[6] that Hudson's lactone rule may also be applied to molecular rotations of polycyclic compounds. The change in molecular rotation from reserpic acid, $[M]_D$ $-692°$ (pyridine) to reserpic acid lactone, $[M]_D$ $+300°$ (pyridine), is $+992°$, therefore the hydroxyl at C-18 is related to D-glyceraldehyde and the absolute configuration of reserpine should be represented by structure VI and not VII.

[6] W. Klyne, *Chemistry and Industry*, 1198 (1954).

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THE TETRAMMINESODIUM ION

Sir:

Compounds of alkali halides and ammonia have been known for some time[1,2] but little information has been available as to the nature of the bonding involved or of their structures. We wish to present a preliminary report of studies made on liquid tetramminesodium iodide, $Na(NH_3)_4I$, which verify the existence of a tetramminesodium ion, $Na(NH_3)_4^+$, of remarkable stability.

The sample was prepared by reaction of anhydrous ammonia with anhydrous NaI and was a thermally stable liquid at 25° with a melting point of 3° and $p_{NH_3} = 420$ mm. at 25°. The ultraviolet spectrum has $\lambda_{min.}$ 309 and $\lambda_{max.}$ 330 and isd istinct from both NaI and ammonia. Infrared and Raman spectra of $Na(NH_3)_4I$ were obtained by standard methods.[3] The absence of characteristic NH_3 deformation frequencies and the observation of a new set of frequencies indicates that this compound has a distinct set of bond properties. The NH_3 deformation frequencies at 950 and 1627 cm.$^{-1}$ have shifted in $Na(NH_3)_4I$ to 1105 and 1525 cm.$^{-1}$ and are surprisingly close to the corresponding CH_3 deformation frequencies of tetramethyl compounds which occur near 1148 and 1448 cm.$^{-1}$ in $Pb(CH_3)_4$. In the Raman spectrum the Na–NH_3 skeletal stretching and deformation frequencies are readily assigned to 435 and 103 cm.$^{-1}$ bands. These frequencies are close to the corresponding frequencies of $Zn(NH_3)_4^{++}$ and $Pb(CH_3)_4$ indicating the existence of rather strong Na–NH_3 bonds.[3,4]

The calculated value of the Na–NH_3 stretching force constant compares favorably with those calculated for $Zn(NH_3)_4^{++}$ and $Pb(CH_3)_4$: ($k_{Na(NH_3{}^{++})_4} = 1.9 \times 10^5$ dynes/cm., $k_{Zn(NH_3{}^{++})_4} = 1.85 \times 10^5$ dynes/cm. and $k_{Pb(CH_3)_4} = 1.87 \times 10^5$ dynes/cm.).

An assignment[3] of frequencies may be made on the basis of a $Na(NH_3)_4^+$ ion and in a manner analogous to that for $Pb(CH_3)_4$, if one assumes that in the Raman spectrum the close doublets have not been resolved and that the weakest bands present in $Pb(CH_3)_4$ have not been observed in $Na(NH_3)_4^+$. The NH_3 rocking frequency which is not present in the infrared spectrum of ammonia and observed at 765 cm.$^{-1}$ in $Pb(CH_3)_4$ appears near 500 cm.$^{-1}$ in $Na(NH_3)_4^+$. The distribution of the NH frequencies in $Zn(NH_3)_4^{++}$ and $Na(NH_3)_4^+$ ions is nearly the same.

The Raman lines observed for the $Na(NH_3)_4^+$ ion were much broader than the corresponding lines observed for $Zn(NH_3)_4^{++}$ and $Cd(NH_3)_4^{++}$ ions,[4] and the presence of other ionic species such as $Na(NH_3)_3^+$ and $Na(NH_3)_2^+$ cannot be completely eliminated.

The observation of a distinct ultraviolet spectrum along with the evidence for a distinct set of bond properties from the vibrational spectrum indicates that the stability of this compound is due to the presence of charge transfer forces involving resonance best illustrated in terms of no-bond and bonded structures such as $[\mathrm{Na{-}NH_3}]$ and $\left[\overset{-}{\mathrm{Na}}{-}\overset{+}{\mathrm{N}}\mathrm{H_3}\right]$.[5] However the presence of broad bands in the Raman spectrum and the observation of a low NH_3 rocking frequency suggests that ion-dipole forces are more important in $Na(NH_3)_4^+$ than in ammonia complexes of the transition metals.

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[1] W. Biltz and W. Hansen, *Z. anorg. allgem. Chem.*, **127**, 1–33 (1922).

[2] M. Picon, *Compt. rend.*, **168**, 825 (1919).

[3] E. R. Lippincott and M. C. Tobin, THIS JOURNAL, **75**, 4141 (1953).

[4] J. L. Silver, Ph.D. Thesis, University of Connecticut, 1953.

[5] R. S. Mulliken, THIS JOURNAL, **64**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

[6] Supported in part by a grant from the Kansas State College Faculty Research Fund.