fore, tempting to suggest that this is because of changes in the overall hybridization of the nitrogen atom as the ring size is increased, *i.e.*, a change of the lone pair orbital from an sp^2 hybrid (in aziridine) toward an sp^3 orbital. It is well established[4] that in cycloalkanes the s character of the carbon–hydrogen bond increases with decreasing ring size. This may allow us to expect that in cyclic amines the s character of the lone pair electrons increases with decreasing ring size and the IP of the nitrogen lone pair will reflect this hybridized nature. To examine the relation between the IP's and the s character of lone pair electrons in cyclic amine, we plotted in Figure 1 the first IP's of cyclic amines against the values of the directly bonded ^{13}C–^1H nuclear spin coupling constants[4a] of the corresponding cycloalkanes. This figure shows that the IP's of lone pair electrons are well correlated linearly with their s character.[5]

It is also tempting to expect some relation between the IP of amines and their basicity. It was reported[6] that in aqueous solution the basicity of cyclic amines falls in the order: azetidine ($pK_a = 11.29$) > pyrrolidine (11.27) > piperidine (11.22) > hexamethylenimine (11.07) > aziridine (8.04). It is apparent that these basicities do not parallel the IP values for cyclic amines; the basicity of azetidine appears to be too strong for its IP value. Recently, Bowers, *et al.*,[7] have determined the relative basicity of cyclic amines in the vapor phase using icr (ion cyclotron resonance) spectroscopy;[8] the basicity falls in the order, piperidine > pyrrolidine > azetidine. Here the basicities correspond well to the trend of IP's in cyclic amines.[9] Therefore, the abnormal feature of the relative basicities of cyclic amines could be attributed to the solvent effect.[10,11] It is also to be noted in Table I that the values of the IP's decrease on going from secondary to tertiary amines. This trend does not parallel the relative strength of basicity.[6,12,13] This could be also attributable to a solvent effect involved in basicity in solution.[10,11]

From the above results and discussion it may be reasonable to conclude the IP values of cyclic amines could be used as a measure of the basicity and the hybridized nature of their lone pair electrons. Similar studies for bicyclic amines are now in progress.

(4) (a) J. J. Burke and P. C. Lauterbur, *J. Amer. Chem. Soc.*, **86**, 1870 (1964); (b) A. Streitwieser, Jr., R. A. Caldwell, and W. R. Young, *ibid.*, **91**, 529 (1969).

(5) This relationship would be acceptable, if we assume that the C–N–C bond angle in cyclic amines is not so different from the C–C–C angle in the corresponding cycloalkanes. This is because the C–C–C angle is directly related to the J_{C-H} value, a measure of s character of the C–H bond: C. S. Foote, *Tetrahedron Lett.*, 579 (1963); K. Mislow, *ibid.*, 1415 (1964).

(6) S. Searles, M. Tamres, F. Block, and L. A. Quarterman, *J. Amer. Chem. Soc.*, **78**, 4917 (1956); H. K. Hall, *J. Phys. Chem.*, **60**, 63 (1956).

(7) M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, Jr., *J. Amer. Chem. Soc.*, **93**, 4314 (1971).

(8) The gas-phase basicity of amines has also been extensively studied by others (see ref 10–13).

(9) The gas-phase basicities of aliphatic amines determined by icr have been related to the N–H bond dissociation energies and the IP's of amines (see ref 11).

(10) E. M. Arnett, F. M. Jones, III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 4724 (1972).

(11) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Amer. Chem. Soc.*, **94**, 4726 (1972).

(12) J. I. Brauman, J. M. Riveros, and L. K. Blair, *J. Amer. Chem. Soc.*, **93**, 3914 (1971).

(13) W. G. Henderson, M. Taagepera, D. Holtz, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *J. Amer. Chem. Soc.*, **94**, 4728 (1972).
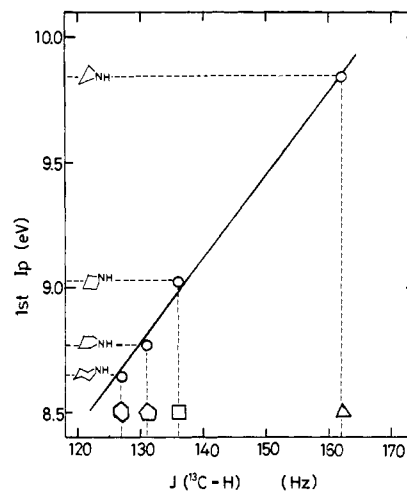
Figure 1. A plot of first IP's against J_{C-H} in cycloalkanes.

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Molecular Structure of 1,6,6a-Trithia(6a-S^{IV})pentalene

Sir:

The trithiapentalenes (I) are substances of unusual composition having aromatic properties. The crystal structures of several of these substances have been investigated by X-ray diffraction with the following important results. In the symmetrically substituted 2,5-
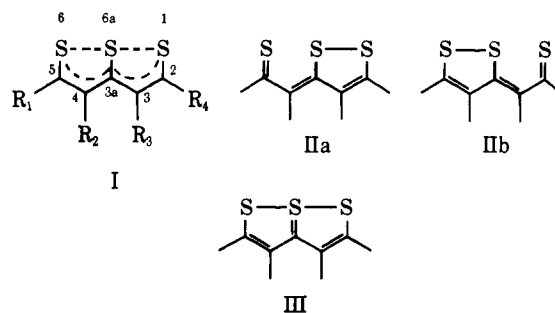
dimethyl compound[1] the distances S_6-S_{6a} and S_1-S_{6a} are equal in length at 2.36 Å, which is about 0.32 Å longer than the sum of the covalent single bond radii, implying important contributions from resonance structures IIa and IIb involving single-bond no-bond resonance. Although the equality of the S–S bonds in this compound has been verified by a reinvestigation,[2] these bonds do not appear to be equal in the 2,5-di-

(1) S. Bezzi, M. Mammi, and C. Garbuglio, *Nature (London)*, **182**, 247 (1958).

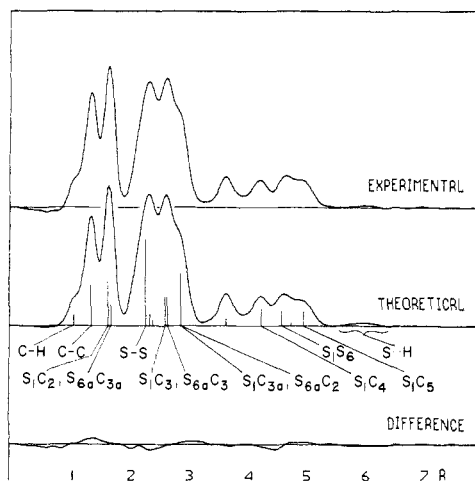(2) F. Leung and S. C. Nyburg, *Chem. Commun.*, 137 (1969).

Figure 1. Radial distribution curves. The curves were calculated from intensity data over the range $0 \leqslant s \leqslant 30.00$, using theoretical data for $s < 2.00$ in the case of the experimental curve, with the convergence coefficient B equal to 0.0020. The theoretical curve is for model A. The distances corresponding to the unlabeled bars may be identified from Table II in the microfilm edition.

Table I. Results for Models of 1,6,6a-Trithia($6a$-S^{IV})pentalene[a,b]

Parameter	A	B	C
r(C–H)	1.111 (0.017)	1.114 (0.019)	1.085 (0.023)
$\langle r$(C–C)$\rangle^c$	1.392 (0.003)	1.393 (0.003)	1.391 (0.003)
Δ(C–C)^d	0	0.057 (0.010)	−0.018 (0.014)
r(S$_{6a}$–C$_{3a}$)	1.736 (0.030)	1.708 (0.028)	1.699 (0.012)
$\langle r$(S–C)$\rangle^e$	1.688 (0.011)	1.698 (0.014)	1.708 (0.011)
Δ(S–C)^f	0	0	0.100
$\langle \angle 3a \rangle^g$	118.3 (0.7)	119.2 (0.8)	119.2 (0.6)
$\Delta(\angle 3a)^h$	0	0	6.8 (0.7)
$\langle \angle 4,3 \rangle^i$	119.7 (0.5)	119.4 (0.5)	119.2 (0.5)
$\Delta(\angle 4,3)^j$	0	0	0
$\langle \angle 5,2 \rangle^k$	119.3 (0.7)	118.7 (0.8)	119.5 (0.7)
$\Delta(\angle 5,2)^l$	0	0	0
$\angle$C$_2$C$_3$H$_3$	122.0	122.0	122.0
R^m	0.0823	0.0859	0.1069

^{a} Distances (r_a) in ångströms; angles in degrees. ^{b} Parenthesized values are 2σ and include estimates of systematic error. ^{c} $[r(C_3$–$C_{3a}) + r(C_2$–$C_3)]/2$. ^{d} $r(C_3$–$C_{3a}) - r(C_2$–$C_3)$. ^{e} $[r(S_1$–$C_2) + r(S_6$–$C_5)]/2$. ^{f} $r(S_1$–$C_2) - r(S_6$–$C_5)$. ^{g} $(\angle 6a3a3 + \angle 6a3a4)/2$. ^{h} $\angle 6a3a3 - \angle 6a3a4$. ^{i} $(\angle 543a + \angle 233a)/2$. ^{j} $\angle 543a - \angle 233a$. ^{k} $(\angle 654 + \angle 123)/2$. ^{l} $\angle 654 - \angle 123$. ^{m} $R = \Sigma w_i \Delta_i{}^2 / \Sigma w_i I_i{}^2$(obsd); $\Delta_i = I$(obsd) $- I$(calcd).

phenyl compound (the difference is about 0.06 Å)[3] and are certainly very different (0.20–0.39 Å) in the unsymmetrically substituted compounds.[4-6] The central C–C bonds of the pentalene chains are 0.04–0.06 Å longer than the terminal bonds and the bond S$_{6a}$–C$_{3a}$ is ∼0.05 Å longer than the other S–C bonds in all compounds. Because the nature and location of the substituents seem to play an important part in the structure of the ring systems of these molecules, we wish to report our electron diffraction results for the parent molecule, 1,6,6a-trithia($6a$-S^{IV})pentalene (I with R = H), in the gaseous state.

The experiments were made with the Oregon State apparatus at a nozzle-tip temperature of 180°, and the data were analyzed in the usual way. Analysis of the experimental radial distribution curve (the final one is shown Figure 1) showed that the molecule was symmetric or nearly so. A nonsymmetric coplanar molecule requires 13 parameters to define its heavy-atom geometry. Because the determination of values for all these was clearly impossible, we limited our least-squares refinements to trial structures comprising symmetric models (C_{2v} symmetry as suggested by I or by IIa + IIb as resonance forms) and unsymmetric models (C_s symmetry) obtained from them by changing some of the more important distances and angles. The parameters chosen to describe the structure are listed in Table I together with the results from refinements of three trial structures: A is a symmetric (C_{2v}) model with all C–C bond lengths equal, B differs from A only in that $r(C_3$–$C_{3a}) = r(C_{3a}$–$C_4) \neq r(C_2$–$C_3) = r(C_4$–$C_5)$, and C is a model of C_s symmetry differing from A in the assumptions $r(S_1$–$C_2) > r(S_6$–$C_5)$ and $r(C_2$–$C_3) = r(C_{3a}$–$C_4) \neq r(C_3$–$C_{3a}) = r(C_4$–$C_5)$.

Model C has some unreasonably small amplitude values ($l_{12} = l_{65} = 0.016$ (0.011)) which, because they

(3) A. Hordvick, Acta Chem. Scand., 22, 2397 (1968). The author suggests the molecule may be symmetrical in the gas phase.

(4) A. Hordvik, E. Sletten, and J. Sletten, Acta Chem. Scand., 23, 1852 (1969).

(5) P. L. Johnson and I. C. Paul, Chem. Commun., 1014 (1969).

(6) S. M. Johnson, M. G. Newton, I. C. Paul, R. J. S. Beer, and D. Cartwright, Chem. Commun., 1170 (1967).

are associated with important distances, suggest it be rejected. Further, the R factors of Table I suggest this model to be significantly poorer than the others, a judgment supported by the poorer agreement between the theoretical curves corresponding to it (not shown) and the experimental curves. This model has substantially different S–S bond lengths ($r(S_1$–$S_{6a}) = 2.257$ Å (0.012), $r(S_6$–$S_{6a}) = 2.460$ Å (0.024)); its poor quality rules out structures of the sort suggested by II.

The agreement between models A and B and experiment is illustrated by the curves of Figure 1. (Although the theoretical curve is for model A, that for B is indistinguishable from it.) Comparison of the parameter values for these models and others not shown reveals the following significant points. (1) Except for Δ(C–C) and $r(S_{6a}$–$C_{3a})$ all geometrical parameters are accurately determined. (2) The variation in the values of Δ(C–C) allows no statement about the relative lengths of the bonds in the pentalene chain, i.e., that they are essentially equal, different with the central pair longer than the peripheral pair, or even different in the sense found in conjugated systems. (3) Models of symmetry C_s with noncoplanar rings are in poorer agreement with experiment than the models of Table I.

It is our conclusion that the best agreement with the electron diffraction data is provided by models of C_{2v} symmetry in the range of parameter space approximately defined by models A and B; small deviations from C_{2v} symmetry cannot, of course, be ruled out. For models in this parameter space the S$_{6a}$–C$_{3a}$, S$_1$–C$_2$, and C–C bonds have bond orders of 1.25–1.40, 1.45, and 1.45–1.75, respectively, according to Pauling's bond-order bond-length criterion.[7] The S–S bonds on the other hand have bond order 0.38–0.44. These bond-order values are in accord with structural representations such as I or as IIa + IIb viewed as resonance forms but not with IIa or III. It is interesting that the amplitude of vibration measured for the S–S bonds is considerably larger than that for the nonbond distance S$_1$···S$_6$; we interpret this remarkable fact as evidence

(7) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 239.

for the "bell-clapper" effect suggested by Gleiter and Hoffmann.[8]

Supplementary Material Available. The important distances and amplitudes for models A, B, and C (Table II), the correlation matrix for model A (Table III), and a listing of the experimental intensity data (Table IV) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-289.

(8) R. Gleiter and R. Hoffmann, *Tetrahedron*, **24**, 5899 (1968).

(9) H. Davy and J. Vialle, *C. R. Acad. Sci., Ser. C*, **275**, 625 (1972).

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Kinetics of Ammonia Detachment from Reduced Cobalt(III) Complexes Based on Conductometric Pulse Radiolysis[1]

Sir:

Pulse radiolysis of aqueous solutions has been increasingly exploited in the study of fast reduction processes[2,3] because (a) it conveniently produces a strong reducing agent, the hydrated electron, e_{aq}, and (b) quantitative reduction can be achieved in less than 1 μsec (depending on the pulse length, rate constant, and the concentration of the reactant) which is a few orders of magnitude faster than in the conventional stopped-flow techniques. We wish to report some observations regarding the kinetics of ammonia detachment from a rapidly reduced cobalt(III) hexaamine and some $Co^{III}(NH_3)_5X$ complexes as well as to demonstrate a research potential of a recently developed alternating current (ac) kinetic conductivity technique coupled to pulse radiolysis in the study of coordination complexes.

The radiolysis of aqueous solutions leads to formation of free radicals and ions[2] with G values (number/100 eV

$$H_2O \rightsquigarrow e_{aq}(2.8), \; OH(2.8), \; H(0.6), \; H_3O^+(2.8) \quad (1)$$
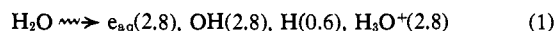
absorbed, after neutralization of the OH⁻ also formed) indicated in parentheses. The formation of e_{aq} and H_3O^+ generates an increase in conductivity of the solution with specific conductance $(e_{aq}) = 198 \; \Omega^{-1}$ equiv⁻¹ cm² and $(H_3O^+) = 350 \; \Omega^{-1}$ equiv⁻¹ cm² (all at 25°). These and other conductivity changes can be easily followed by kinetic conductivity as a function of time.[4]

(1) Supported in part by NIH Grant GM 13 557 and AEC contract AT-(40-1)-3408.

(2) See, *e.g.*, E. J. Hart and M. Anbar, "The Hydrated Electron," Wiley-Interscience, New York, N. Y., 1970; F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1968.

(3) G. P. Venerable, E. J. Hart, and J. Halpern, *J. Amer. Chem. Soc.*, **91**, 7538 (1969).

(4) J. Lilie and R. W. Fessenden, *J. Phys. Chem.*, **77**, 674 (1973).
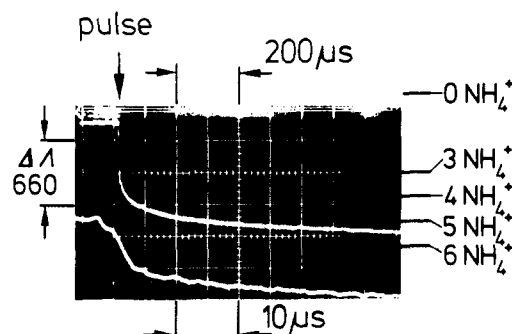
Figure 1. Pulse radiolysis of 5 × 10⁻⁴ M Co(NH₃)₆³⁺, 0.1 M t-BuOH, pH 4.0, Ar purged. Conductivity changes due to the following reactions: (a) Co(NH₃)₆³⁺ + (e_{aq}, H⁺) $\rightsquigarrow$ Co(NH₃)₆²⁺ + H⁺; ΔΛ = 290 Ω^{-1} cm²; (b) Co(NH₃)₆²⁺ + H⁺ → Co²⁺ +6NH₄⁺ (−5H⁺); ΔΛ = −1360 Ω^{-1} cm². Reaction b takes place stepwise.

Briefly, a cell with two pairs of platinum electrodes (one pair for compensation) is irradiated with 1-μsec pulses of 1.6 MeV electrons from a Van de Graaff generator. The radiation induced changes (reaction 1 and subsequent reactions of the primary species) can be followed simultaneously by optical absorption and conductivity measurements. The 10-MHz input allows response in the 1 μsec region. Conductivity changes induced by the formation or loss of 10⁻⁷ M ions can be quantitatively followed in solutions of up to 10⁻² M ions. Tetranitromethane was used as a dosimeter. The output signals are recorded on a tape and the kinetic data are evaluated by a computer. All experiments were performed at the Hahn-Meitner-Institute.
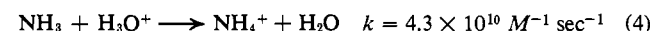
Many Co(III) complexes react with e_{aq} at a diffusion controlled rate,[2] *e.g.*

$$e_{aq} + Co(NH_3)_6^{3+} \longrightarrow Co(NH_3)_6^{2+}$$

$$k = 8.0 \times 10^{10} \; M^{-1} \; sec^{-1} \quad (2)$$
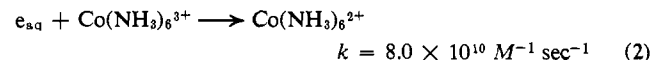
Since the resulting Co(II) complex is unstable, it decomposes with an overall stoichiometry

$$Co(NH_3)_6^{2+} \xrightarrow{H_2O} Co(H_2O)_6^{2+} + 6NH_3 \quad (3)$$
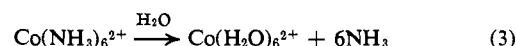
Under our experimental conditions (pH 4.0–4.5) the ammonia molecules are rapidly protonated[5] ($\tau < 1$ μsec)

$$NH_3 + H_3O^+ \longrightarrow NH_4^+ + H_2O \quad k = 4.3 \times 10^{10} \; M^{-1} \; sec^{-1} \quad (4)$$

and a decrease in conductance results since H_3O^+ ($\Lambda = 350 \; \Omega^{-1}$ equiv⁻¹ cm²) is replaced by NH_4^+ ($\Lambda = 75 \; \Omega^{-1}$ equiv⁻¹ cm²). Hence, the overall time resolution for the detection of the ligand detachment was about 1 μsec. In Figure 1 conductivity changes resulting from reaction 2 are presented as a function of time. It is clear that reaction 3 takes place in four distinguishable steps. The first step is a very fast elimination of the first three ammonia ligands.

$$Co(NH_3)_6^{2+} \longrightarrow Co(NH_3)_3^{2+} + 3NH_3 \quad k > 10^6 \; sec^{-1} \quad (5)$$
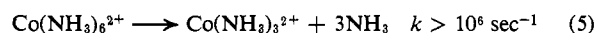
The individual steps are too fast (<2 μsec) and cannot be separated by the present technique. Such high values for the NH₃ elimination are expected from measurements of the ammonia exchange rate of concentrated aqueous ammonia solutions of Co^{II} where a value of $k = 5 \times 10^6$ sec⁻¹ has been measured for the exchange of one NH₃ by another.[6]

(5) M. Eigen, *Angew. Chem.*, **75**, 489 (1963).

(6) R. Murray, S. F. Lincoln, H. H. Glaeser, H. W. Dodge, and J. P. Hunt, *Inorg. Chem.*, **8**, 554 (1969).