and ΔH_{soln} is the heat of solution per mole. In these computations, ΔH is assumed to be constant and activity coefficients of potassium halides approach unity.[9] Figure 1 gives the best least-squares fit of the solubility data plotted as ln (molality) against the reciprocal of the absolute temperature.

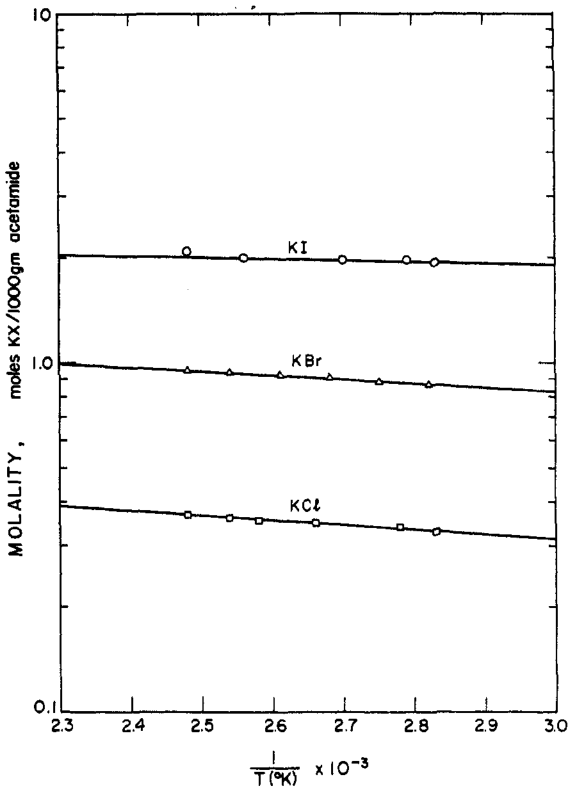

Figure 1.—Plot of ln (molality) of potassium halide salts in fused acetamide against reciprocal temperature.

The heats of solution of potassium halides in fused acetamide are 631, 544, and 163 cal/mol for KCl, KBr, and KI, respectively. The order of the observed heats of solution is in the reverse order of the corresponding heats of solution of these salts in water.[8] These data indicate that the much larger potassium halide solubilities in water correspond to smaller heats of solution. In formamide at 25° the corresponding heats of solution, as given by Held and Criss,[10] are 2220 cal/mol for KI, 820 cal/mol for KCl, and 230 cal/mol for KBr.

In essence, the facts that potassium halide salts are readily soluble and that the acetamide has a high[11] dipole moment of 3.7 D suggest that considerable solvation occurs. From these results and others,[12] acetamide should be rated as an unusually good electrolytic solvent for inorganic salts and their reactions, particularly over the elevated temperature range between 80 and 130°.

Acknowledgment.—This work was supported in part by the Stanford University Center for Materials Research.

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[9] J. Hildebrand, "Solubility," Reinhold, New York, N. Y., 1936.

[10] R. Held and C. Criss, *J. Phys. Chem.*, **69**, 2611 (1965).

[11] J. Stout and L. Fischer, *J. Chem. Phys.*, **9**, 163 (1941).

[12] C. French and K. Glover, *Trans. Faraday Soc.*, **51**, 1427 (1955).

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The Electronic Structure of N,N′-Bis[pentaammineruthenium(II,III)]-pyrazine(5+)

BY JOEL H. ELIAS AND RUSSELL S. DRAGO*

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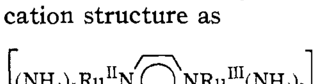
Creutz and Taube[1] have reported the synthesis of the complex *N,N′*-bis[pentaammineruthenium(II,III)] pentakis(*p*-toluenesulfonate) trihydrate to which they assigned the cation structure as


$$\left[(NH_3)_5Ru^{II}N\langle C_4H_4\rangle NRu^{III}(NH_3)_5\right]^{5+}$$

Very rapid electron transfer was reported to occur converting the Ru(II) to Ru(III) and the Ru(III) indicated above to Ru(II). They interpreted a band at 1570 mμ in the near-ir spectrum of the above complex as arising from an electron-exchange transition, which they described as [2,3] → [3,2]* and, from the energy of this transition, they calculated a rate of electron exchange of 3×10^9 sec^{-1}. In a complex molecule of this sort, the near-ir transition could arise from some other source, *vide infra*, so we have considered several alternative possibilities for the bonding in this complex: (a) Creutz and Taube's structures with electron exchange slow on the nmr time scale, (b) Creutz and Taube's structures with rapid electron exchange, (c) two Ru(III)'s bridged by a pyrazine radical anion, (d) a molecular orbital description in which the metal ion and pyrazine-filled π mo's are mixed and the unpaired electron is mainly but symmetrically distributed over the two cations, and (e) a similar mo scheme in which the interaction is essentially with the π^* mo's of pyrazine. It should be realized that both (d) and (e) could be occurring simultaneously, and our conclusion is related to which one dominates the energy level ordering.

In an attempt to shed further light on the electronic structure of this most interesting system, we have studied the isotropic ^{1}H nuclear magnetic resonance shifts of this complex. Other than the solvent and anion resonances, we observed three peaks shifted downfield from internal TMS. The results are given in Table I. The assignments are based on the line widths and comparison with the isotropic spectra of the pentaammine halides of Ru(III).[2] The area of the cis ammine resonance is much larger than any of the other resonances, and this aids in its identification.

The structures described under (a) above can be eliminated on the basis of the observed spectrum since, for slow electron exchange, we would expect to see six separate resonances. The ammonias on the ruthenium(II) would be expected to be sharper than those observed and easy to detect.

Next, we shall consider the possibility of having a bridging radical anion (c) in which the electron is in an empty π^* ligand orbital. The value of the ^{1}H hyperfine coupling constant for the pyrazine anion is

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[1] C. Creutz and H. Taube, *J. Amer. Chem. Soc.*, **91**, 3988 (1969).

[2] J. A. Stanko and N. Matwiyoff, private communication.

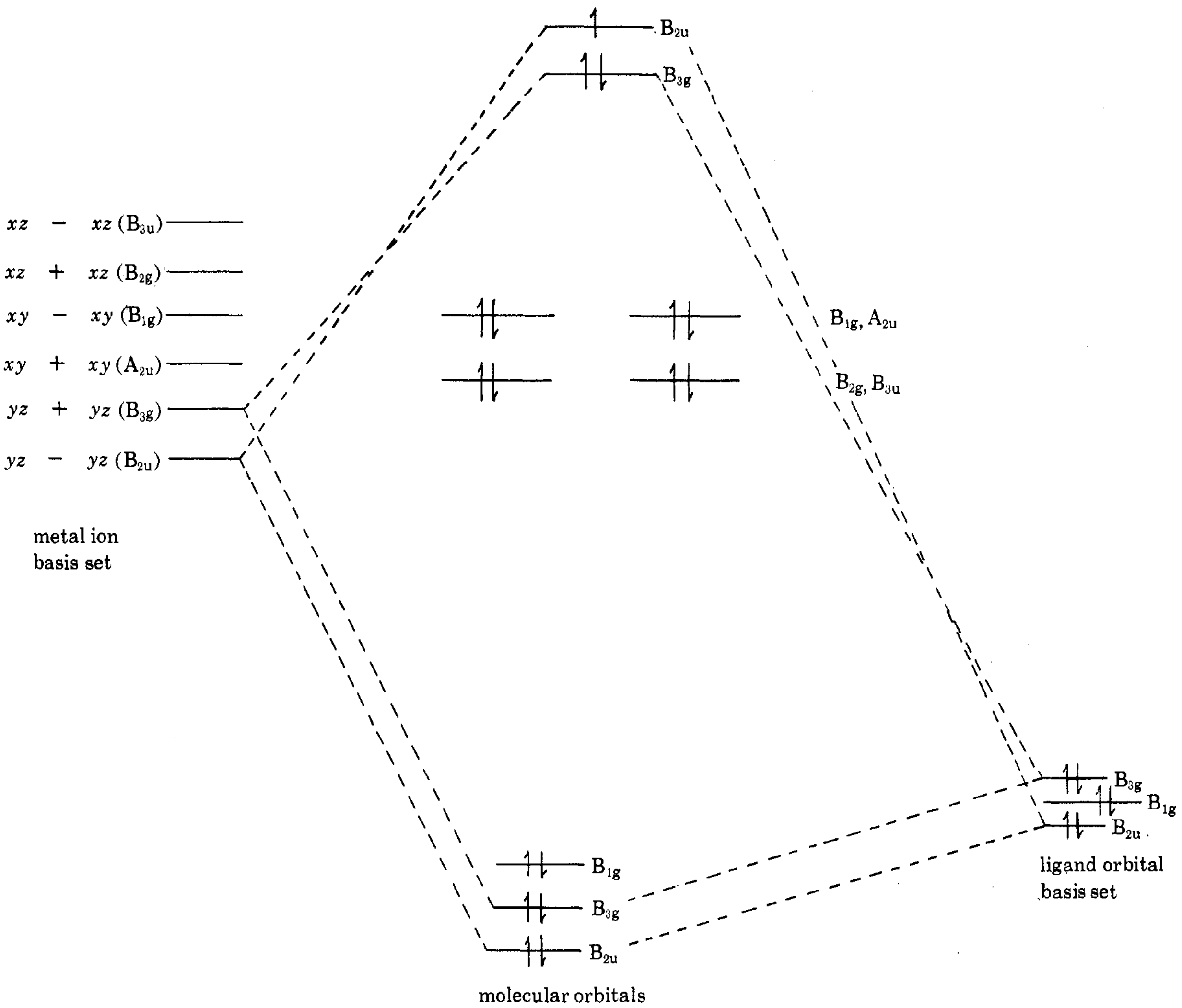

Figure 1.—Metal orbital–pyrazine π-orbital mixing (ligand energy ordering is that obtained from our EHT calculation).

known from electron paramagnetic resonance studies[3] to be 2.6 G. From eq 1 we see that this would give

$$\frac{\Delta\nu}{\nu} = \frac{-ag_{\mathrm{av}}{}^2\beta^2S(S+1)}{g_{\mathrm{N}}\beta_{\mathrm{N}}(3kt)} \qquad (1)$$

rise to a value of $\Delta\nu \approx +19{,}000$ Hz for the Fermi contact shift. Although the sign of the coupling constant is not known from esr, an upfield proton contact shift is expected because the protons are orthogonal to the π^* orbital. In addition to an expected shift of +19,000 Hz from an electron in this antibonding orbital, an upfield shift would be expected for a pyrazine coordinated to Ru(III) by analogy to shifts in pyridine[4] and tris-bipyridyl complexes.[5] In these systems, spins in metal orbitals of π symmetry cause upfield shifts of the order of magnitude of ~2500 Hz.

An order of magnitude estimate of the pseudocontact contribution was made by assuming a complex structure based on the reported structure of the pyrazine molecule[6] and a metal–ligand distance of 2.0 Å for Ru–N from a structure[7] of $[\mathrm{Ru(NH_3)_5Cl}]\mathrm{Cl_2}$.

The elements of the g tensor are those measured by Treitel[8] ($g_{\parallel} = 2.04$, $g_{\perp} = 2.32$). The dipolar shifts calculated from this data are reported in Table I.

TABLE I

OBSERVED SHIFTS AND ESTIMATED DIPOLAR SHIFTS

$\Delta\nu_{\mathrm{obsd}}$,[a] Hz	$\Delta\nu_{1/2}$, Hz	Assignment	Dipolar shift (calcd), Hz Near[b]	Far[b]	Av[c]
−1,910	320	Pyrazine	287	164	225
−7,620	1100	Cis ammine	−1006	66	−470
−12,800	1100	Trans ammine	1539	37	788

[a] At 100 MHz in $(\mathrm{CD_3})_2\mathrm{SO}$ and 29°, referenced to TMS. At 100 MHz, the pyrazine proton resonance in $\mathrm{CDCl_3}$ occurs at −860 Hz relative to TMS. [b] Calculated values based on slow electron exchange. Near protons are adjacent to Ru(III); far protons are adjacent to Ru(II). [c] Average values assuming rapid electron exchange.

From these results, it can be seen that there is no way to account for the observed shift of −1910 Hz with the model of the pyrazine negative ion bridge. If there were three unpaired electrons corresponding to an unpaired electron with spin up in the pyrazine π^* orbital, a huge upfield contact shift would have been observed. This conclusion is in agreement with a measured magnetic moment of 2.23 BM at room tem-

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(3) K. F. Paulus and J. R. Rowlands, *Proc. Chem. Soc., London*, 60 (1962).

(4) R. E. Cramer and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 66 (1970).

(5) R. E. DeSimone and R. S. Drago, *ibid.*, **92**, 2343 (1970).

(6) V. Schomaker and L. Pauling, *ibid.*, **61**, 1769 (1939).

(7) C. K. Prout and H. M. Powell, *J. Chem. Soc.*, 137 (1962).

(8) Private communication from Professor H. B. Gray (I. M. Treitel, Ph.D. Thesis, California Institute of Technology, 1971).

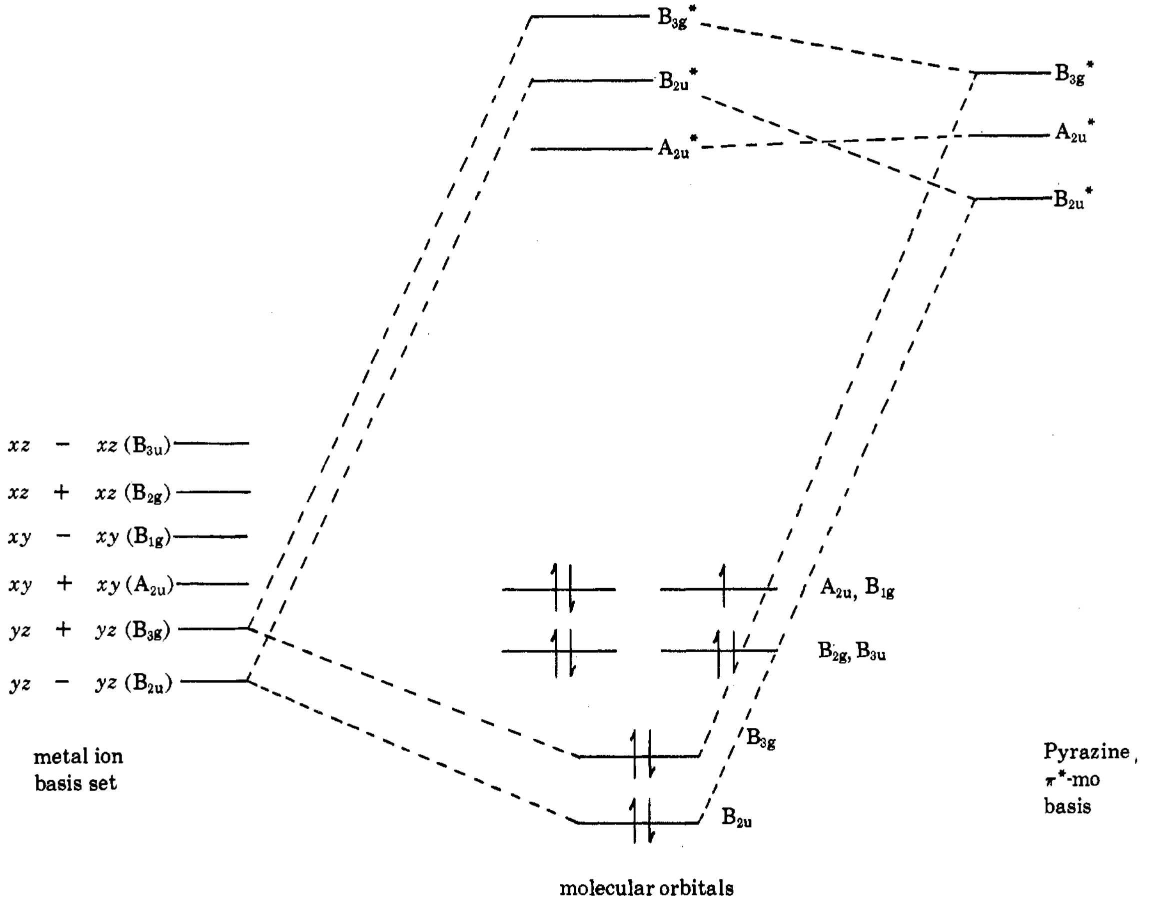

Figure 2.—Metal orbital–pyrazine π^*-orbital mixing (the π^*-energy ordering is that obtained from our EHT calculation).

perature.[8] Furthermore, the contact shift enables us to eliminate a structure in which the unpaired electron in the π^* orbital has opposite spin to that on the metal because a much larger downfield shift would have been observed.

Next, we shall consider a molecular orbital model which results when one metal orbital on each ruthenium is interacting with filled π orbitals of the pyrazine. The mo scheme in Figure 1 results from a consideration of those orbitals on ruthenium which contain the electrons in this model, *i.e.*, those from the t_{2g} set in O_h symmetry. The orbitals with symmetry for σ interaction with NH_3 and pyrazine have been omitted. Here the N–Ru–N bond is defined as the z axis and the ring plane is xz. This scheme puts the unpaired electron in a molecular orbital which has nearly equal contributions from both metals and some ligand character. The next lowest energy, filled set of molecular orbitals is essentially composed of metal orbitals. Regardless of the extent of mixing, an mo calculation on a complex of this symmetry would give rise to mo's, each of which has equal contributions from each ruthenium basis orbital. This electronic configuration would make the two rutheniums equivalent but would place up spin in the π system of pyrazine which should give rise *via* spin polarization to an upfield shift in the proton resonance. Since the calculated dipolar shift is also positive, we cannot account for the observed negative isotropic shift with this model, and it can be rejected.

Next, we shall consider the consequences of a π-back-bonding interaction. The magnitude of this effect could be slight or large just as long as it is great enough to lower the energy of the d_{yz} orbital set. This has no bearing on our discussion, for we cannot draw any conclusions on the magnitude of the lowering of d_{yz} from our studies. The molecular orbital scheme formed by interacting the pyrazine π system and metal orbitals is illustrated in Figure 2. The π-back-bonding interaction lowers the energy of the former d_{yz} orbitals so the unpaired spin ends up in a molecular orbital that is essentially constituted of equal amounts of each ruthenium d_{xy} orbital. Even if the d_{xy} orbital of a ruthenium atom is not involved in extensive overlap with ligand orbitals or the d orbitals of the other ruthenium, the two ruthenium d_{xy} orbitals contribute equally to each of these molecular orbitals in this symmetry. It is of interest to examine the results of our SCC extended Hückel calculations[9] (EHT) on pyrazine which are reported in Table II. Here it is seen that the A_{2u} π^*

TABLE II

RESULTS OF AN SCC CALCULATION ON PYRAZINE

No.	E	N_1 ϕ_1	C_2 ϕ_2	C_3 ϕ_3	N_4 ϕ_4	C_5 ϕ_5	C_6 ϕ_6	
11	−6.10	−0.49	0.54	−0.54	0.49	−0.54	0.54	ψ_6 (B_{3g})
12	−8.40		−0.59	0.59		−0.59	0.59	ψ_5 (A_{2u})
13	−9.85	0.68	−0.28	−0.28	0.68	−0.28	−0.28	ψ_4 (B_{2u})
14	−11.35							σ
15	−12.47							σ
16	−13.03	−0.55	−0.25	0.25	0.55	0.25	−0.25	ψ_3 (B_{3g})
17	−13.58		−0.45	−0.45		0.45	0.45	ψ_2 (B_{1g})
18	−13.80							σ
19	−14.87							σ
20	−15.00	0.28	0.36	0.36	0.28	0.36	0.36	ψ_1 (B_{2u})

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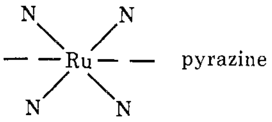
(9) For a complete description, see R. E. Cramer and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 4790 (1968).

orbital with appropriate symmetry to overlap the d_{xy} basis set orbitals has nodes at the nitrogens. Very poor overlap is expected between the pyrazine π^* molecular orbitals and the ruthenium d_{xy} orbitals. Thus, a significant amount of unpaired spin would not be directly delocalized (*i.e.*, very little up spin in the π^* system), so an upfield Fermi contact shift would not arise at the protons. Instead, spin polarization of the paired electrons in B_{2u} and B_{3g} by the unpaired electron would increase positive spin density on the ruthenium in B_{2u} and B_{3g} and increase negative spin density in the pyrazine π system. The mechanism is similar to the spin polarization of the paired electrons in a C–H bond by an unpaired electron in an orthogonal carbon p orbital. This spin polarization would place up spin on the proton and be expected to give rise to a small downfield Fermi contact contribution. This would have to be about 1000 Hz larger than and in the opposite direction to the pseudo contact shift (Table I) to account for the magnitude of the shift expected from pyrazine coordinated to a diamagnetic ligand. In this model the low-energy electronic transition reported[1] at 1570 mμ for the $5+$ ion would be attributed to a d–d transition involving the B_{3g} or B_{2u} and A_{2u} or B_{1g} orbitals. The similarity of the remaining bands of the $5+$ species with those of the $4+$ is not surprising in view of the reported[10] similarity of the hexaammines of Ru(II) and Ru(III).

We have also considered the possibility that steric repulsions between the pyrazine and ammine protons force the molecule into a skewed configuration with the plane of the pyrazine molecule bisecting the H_3N–Ru–NH_3 planes



Such a configuration leads to mo schemes which are analogous to those in Figure 1 and 2 and do not affect our conclusions. It is likely, however, that rotations about the metal–nitrogen bond axes in this complex are rapid on the nmr time scale.

These models for the bonding would approach the Creutz–Taube description (b) if, in the course of undergoing molecular vibrations, the potential energy curve for the appropriate normal mode had a minimum when the ammonia nitrogens around one ruthenium were stretched and those around the other ruthenium compressed. This would result in an unequal contribution from each ruthenium to the A_{2u} and B_{1g} mo's. The larger contribution by one of the rutheniums to the mo containing the unpaired electron would make that ruthenium more like Ru(III) and the dynamic nature of the vibration would very rapidly change a given ruthenium from one extreme to the other. With this model, the whole range of fractional oxidation states is covered depending only on where the minimum in the potential energy curve for the vibration occurs. We have no information available to support or reject this possibility.

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Chemistry of Fluorinated Derivatives of Azodiformamidine[1]

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Earlier we reported that the solid fluorination of azodiformamidine dinitrate yielded the new highly fluorinated azo compounds difluorotetrakis(difluoramino)azomethane, $(NF_2)_2CFN{=}NCF(NF_2)_2$, I, [bis(difluoramino)fluoromethylazo]trifluoroformamidine, $(NF_2)_2CFN{=}NC({=}NF)NF_2$ (two isomers), IIa and b, and hexafluoroazodiformamidine, $NF_2C({=}NF)N{=}NC({=}NF)NF_2$ (three isomers), IIIa–c.[3] This report is concerned with the chemistry of these compounds and describes the preparation of several unique azo derivatives.

The thermal reaction of I with carbon monoxide yielded tetrafluoroazodimethylenimine, IV, as the principal product

$$(NF_2)_2CFN{=}NCF(NF_2)_2 \xrightarrow[180^\circ]{CO} FN{=}CFN{=}NCF{=}NF \quad (IV)$$

The photolysis of IV with a sunlamp produced perfluoromethylenimine and cyanogen fluoride providing further confirmation of the structure. The reaction of either IIa or IIb with carbon monoxide at lower temperature gave two isomers of (trifluoroguanylazo)difluoromethylenimine, Va and b.

$$(NF_2)_2CFN{=}NC({=}NF)NF_2 \xrightarrow[120^\circ]{CO} FN{=}CFN{=}NC({=}NF)NF_2 \quad (Va,\ b)$$

The probable stereochemical configurations for these compounds together with pertinent nmr and ultraviolet spectral data are presented in Table I. The assignments are based upon considerations discussed earlier in connection with the structures of the isomers of II and III.[3] At higher temperature, the reaction of IIa or IIb with carbon monoxide also produced IV. It should be noted that in each of the above-mentioned cases, the reaction involves the effective elimination of one or two molecules of nitrogen trifluoride and the formation of a more highly conjugated system.

The ability of IIa or IIb to undergo addition reactions was found to depend upon the basicity of the attacking reagent. For example, no reaction occurred with hydrogen chloride, hexafluoroisopropyl alcohol, isocyanic acid, or water at ambient or lower temperature. A partial reaction occurred with methanol but the resulting adduct was very unstable. The low-temperature reaction of IIa or IIb with ammonia produced an orange solid which decomposed upon warming. However, fluorination of this material at −110° produced

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(1) The experimental work described herein was conducted prior to May 30, 1967 and was supported by the Advanced Research Projects Agency through the Army Research Office (Durham) under Contract DA-31-124-ARO(D)-179.

(2) To whom all correspondence may be directed at the Department of Pharmaceutical Chemistry, College of Pharmacy, Medical University of South Carolina, Charleston, S. C. 29401.

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