that of a right-handed helix.[11] However, the interpretive basis for this type of calculation is that the protein consists of two kinds of conformational regions, one having the rotatory properties of a right-handed α-helix, the other having those of a random polypeptide. If this interpretation is correct, the same linear combination of rotations (13% helix, 87% random coil) should account for the dispersion at wave lengths other than 233 mμ. This is not the case with RNase. In particular the low helical content predicted from the amplitude of the Cotton effect at 233 mμ cannot account for the swing to positive rotations at lower wave lengths. It is our interpretation that the negative Cotton effect provides evidence for the presence of right-handed α-helices in RNase but that the simple two-state model does not lead to a consistent explanation of the observed dispersion, so that a meaningful helix content cannot be calculated. Experiments at lower wave lengths, which would help to clarify this situation, are not feasible with present apparatus.

[11] P. Doty, *Coll. Czechoslov. Chem. Commun.*, **22**, Spec. Issue, 5 (1957).

[12] Fellow of the National Foundation.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF OREGON STEVEN B. ZIMMERMAN[12]
EUGENE, OREGON JOHN A. SCHELLMAN

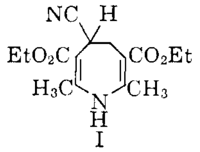
RECEIVED APRIL 28, 1962

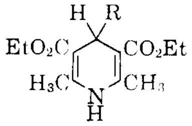
2.7-DIMETHYLAZATROPONE-4

Sir:

We recently described the ring-expansion of II, R = CH_2Cl, to diethyl 2,7-dimethyl-4-cyano-4,5-dihydro-1H-azepine-3,6-dicarboxylate, I.[1] During dehydrogenation studies, we treated I, as well as several dihydropyridines, with sodium nitrite in glacial acetic acid.[2] Some dihydropyridines (*e.g.*, II, R = CH_3) gave the expected pyridine derivatives but II, R = CH_2Cl, yielded the oxime, III (analysis, ultraviolet, infrared and n.m.r. spectra and formation of benzoate) and I afforded a white crystalline solid (15.8%), $C_{14}H_{17}NO_5$, m.p. 119–120° (λ_{max}^{EtOH} 219 (ε 35,600), 249 (infl. ε 11,400) and 296 mμ (ε 9,400)) which had no NH stretching band in the infrared. The n.m.r. spectrum[3] of this compound (in $CHCl_3$ solution) showed that it had two non-equivalent ethyl esters, two methyl groups (7.07, 7.17 τ) and one other single proton (1.25 τ). These signals are all shifted to low field relative to starting material and together with the position of absorption of the single proton, suggest a ring current and hence aromaticity[4] of this product, which we believe, therefore, to be IV, R = COOEt. Compound IV, R = COOEt, now has been obtained directly from II, R = CH_2Cl, by prolonged treatment with aqueous ethanolic potassium cyanide (0.5 mole KCN/mole II, R = CH_2Cl), and chromatography of the oily product on alumina.

Hydrolysis of IV, R = COOEt, with caustic soda yielded a diacid (94%) which was decarboxylated with copper bronze at 320°[5] to give a colorless liquid (85%), C_8H_9NO, (λ_{max}^{EtOH} 217 (ε 13,370), 250 (ε 6,450), 257 (ε 5,920) and 290 mμ (ε 8,790)), showing no NH stretching band in the infrared but having strong absorption at 1613 cm.$^{-1}$ which we ascribe to the "carbonyl" frequency.[6] This product gave a crystalline picrate,[7] m.p. 128° (dec.). The n.m.r. spectrum (in CH_2Cl_2) of this decarboxylated material showed the presence of two methyl groups (7.41, 7.53 τ) and three other protons [2.36, 3.02 (doublet, J = 7.9 c.p.s.) and 3.69 τ] and this is consistent with structure IV, R = H. There appeared to be no "meta" or "para" interaction[8] between the ring protons, but the signal at 3.69 τ was a close quartet, J = 0.8 c.p.s., clearly by interaction with the higher field methyl group (a doublet, J = 0.8 c.p.s.).


I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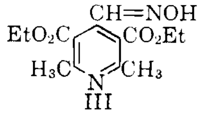
III


IV

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[2] E. Benary and G. Löwenthal, *Ber.*, **55**, 3429 (1922).

[3] Determined at 60 Mc./sec. on an A.E.I. RS 2 instrument with tetramethylsilane as internal reference.

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[8] H. S. Gutowsky, C. H. Holm, A. Saika and G. A. Williams, *J. Am. Chem. Soc.*, **79**, 4596 (1957).

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DEPARTMENT OF CHEMISTRY E. BULLOCK
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RECEIVED MARCH 19, 1962

NUCLEAR MAGNETIC RESONANCE SPECTRA OF SOME HYPOFLUORITES

Sir:

The n.m.r. spectra of F_2, OF_2, CF_3OF, SF_5OF, and SO_3F_2 were taken to see how the hypofluorite resonances of the hypofluorites compared with elemental fluorine and with each other. At the same time it was desirable to observe coupling constants between different types of fluorine atoms in the hypofluorites and to gain additional information concerning molecular structure.

In Table I is presented the order into which the n.m.r. resonances of the hypofluorite fluorine atoms of the hypofluorites fall along with the various coupling constants and chemical shifts observed. Sulfur hexafluoride, because of its ready availability and its ability to dissolve all substances mentioned here, was chosen as internal reference. The data suggest that the charge of fluorine in the -OF group is not positive, but instead, somewhat negative.

TABLE I

CHEMICAL SHIFTS AND COUPLING CONSTANTS FROM NUCLEAR MAGNETIC RESONANCE SPECTRA AT 40 MC.

Substance	Chemical shift, δ, compared to SF_6 as zero[a]		Spin-spin coupling constant, J (c.p.s.)	
	For F_2 or OF (c.p.s)	For SF or CF (c.p.s)		
F_2	−14,620			
OF_2	−8,680			
			Between	
FSO_2OF	−7,500	SF 850	(SO_2F and OF)	6.1
SF OF	−5,250	SF^b 70.0	(SF^b and OF)	0.0
		SF_4 145.6	(SF_4 and OF)	17.4
			(SF_4 and SF^b)	155.0
CF_3OF	−3,700	CF_3 5140	(CF_3 and OF)	33.2

[a] Values are positive in the direction of increased magnetic field strength. In changing from high concentration to infinite dilution in SF_6 solution the SO_3F_2 resonance absorptions change about 15 cycles upfield with respect to the SF_6; SF_5OF absorptions change even less. Dilute SF_6 solutions of the other substances were used and not extrapolated to infinite dilution. [b] Apex fluorine atom resonance in $-SF_5$ group.

All spectra obtained in this work were simple, following first-order intensity rules except for SF_5OF. F_2 and OF_2 possessed single resonances, CF_3OF gave a large doublet for the CF_3 group and a smaller quadruplet for the −OF resonance as reported by Ogg,[1] and SO_3F_2 gave two equal-sized doublets as reported before.[2] Previously, the spectrum of SF_5OF was reported to consist of six resonances for the −OF group and a doublet for the $-SF_5$ group and was considered to indicate the five fluorine atoms in the $-SF_5$ group were magnetically equivalent.[2] With the higher resolution used in the present research, a fine structure was obtained indicating that the five fluorine atoms are not magnetically equivalent. This also has been found to be the case in other pentafluorosulfur compounds.[3,4] The spectrum is shown in Fig. 1.

With the aid of a generalized seven-spin program[5] for the IBM 709 high-speed digital computer a reasonable match between the experimental spectrum of SF_5OF and the computed spectrum was realized. The computation assumed a AB_4X spin system which corresponds to a square pyramid orientation for the fluorine atoms of the $-SF_5$ group. The fact that one fluorine atom in the $-SF_5$ group was distinctly different from the other four invalidates evidence for fluorine exchange within the $-SF_5$ group furnished by the previous study.[2] Figure 1 also gives the computed n.m.r. spectrum of SF_5OF. Even the high resolution obtained in this study was insufficient to resolve all resonances in the SF_5OF spectrum. By grouping lines that are very close together the calculated spectrum is found to agree very well with the experimental spectrum.

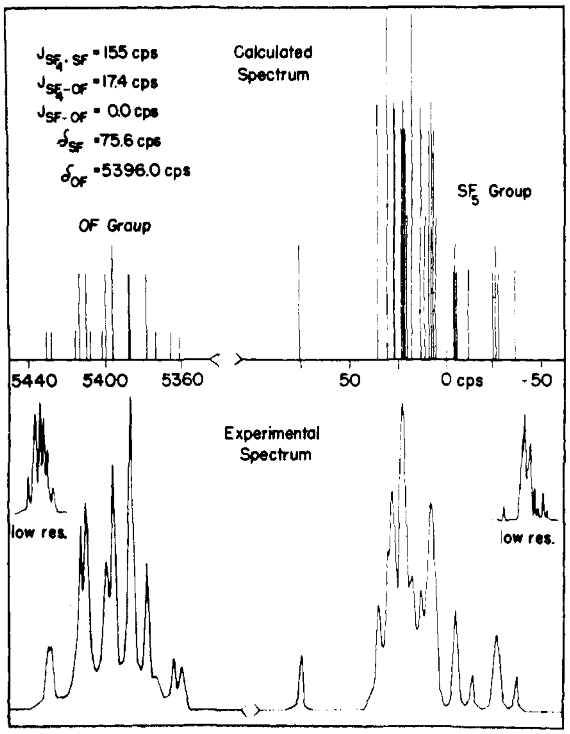

Fig. 1.—Spectrum of SF_5OF at 40 Mc. both experimental and calculated. Low resolution parts of the spectrum are given on the left and right sides of the figure. Planar fluorine atoms of $-SF_5$ group are given zero chemical shift.

Experimental

Sample tubes were made from 5-mm. Pyrex glass tubing of 1-mm. wall thickness. Each tube was filled by condensing together sulfur hexafluoride and the substance to be studied. After the tube had been sealed hermetically it was tested for strength by placing it in water (in a hood) at 32°. Some tubes exploded from pressure. Those which did not were used.

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(1) R. A. Ogg, Jr., Paper presented at the 126th National American Chemical Society Meeting, New York, N. Y., September, 1956.

(2) F. B. Dudley, J. N. Shoolery and G. H. Cady, *J. Am. Chem. Soc.*, **78**, 568 (1956).

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(4) C. I. Merrill, S. M. Williamson, G. H. Cady and D. F. Eggers, Jr., *Inorg. Chem.*, **1**, 215 (1962).

(5) Program provided by Prof. K. B. Wiberg, University of Washington.

Acknowledgment.—This work was performed under contract with the Office of Naval Research. The n.m.r. spectra were obtained with the assistance of B. J. Nist.

CONTRIBUTION FROM THE
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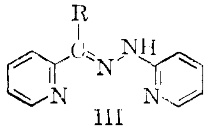
GEORGE H. CADY
CLAUDE I. MERRILL

RECEIVED OCTOBER 14, 1961

NEW AROMATIC-TYPE CHELATE COMPOUNDS

Sir:

We wish to report new aromatic-type oil-soluble very stable chelate compounds which appear to have important potentialities. The hydrazones (I) obtained by interaction of N-heterocyclic hydrazines, similar in type to 2-pyridylhydrazine, with heterocyclic aldehydes and ketones, similar in type of the 2-acyl pyridines, can function as tridentate chelating agents; whilst the osazones (II) derived from such hydrazines and α-dicarbonyl compounds can function as quadridentates.[1] Thus from 1,3-bis-(2′-pyridyl)-1,2-diazaprop-2-ene (III, R = H) the red diamagnetic iron(II) salt IV (R = H, Me = Fe, X = ClO_4, $n = 2$, $m = 2$) has been prepared.[1] We now report that addition of alkali to its solution in aqueous ethanol changes the color to green and the green crystalline non-conducting paramagnetic (1.8 B.M. at 18°) complex V (R = H, Me = Fe, $m = 1$) separates (Calcd. for $C_{22}H_{18}N_8Fe.H_2O$: C, 56.4; H, 4.3; Fe, 11.9. Found: C, 56.2; H, 4.1; Fe, 12.1). Similar non-conducting complexes from I (R = H) and almost all of the bivalent transition metals can be prepared readily; for example, the brown nickel(II) complex V (R = H, Me = Ni, $m = 1.5$. Calcd. for $C_{22}H_{18}N_8Ni{\cdot}1.5H_2O$: C, 55.0; H, 4.4; Ni, 23.3. Found: C, 54.8; H, 4.4; Ni, 22.8).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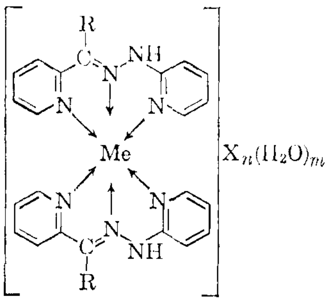

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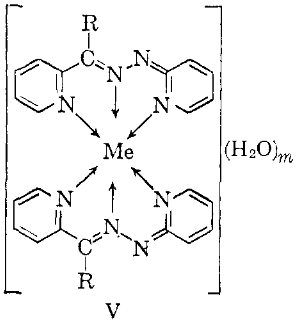

V

We have prepared very many neutral complexes of similar type from, for example, the 1-pyridylhydrazones, 2-pyrimidylhydrazones and 3-methyl-2-pyrazinyl hydrazones of such aldehydes as 6-methyl-pyridine-2-aldehyde, quinoline-2-aldehyde, isoquinoline-1-aldehyde, isoquinoline-3-aldehyde and quinoline-8-aldehyde, and of such ketones as the series III (R = CH_3 to R = n-C_6H_{13}) and metals such as iron, nickel cobalt, cadmium, zinc, manganese, copper—(in fact, almost all of the transition metals). A typical example is the red neutral zinc(II) complex from the α-pyridylhydrazone of 6-methyl-pyridine-2-aldehyde (colorless needles, m.p. 208–210°. Calcd. for $C_{12}H_{12}N_4$: C, 67.9; H, 5.7; N, 26.4. Found: C, 67.7; H, 5.7; N, 26.8) which crystallized in red needles from benzene–petroleum ether (calcd. for $C_{24}H_{22}N_8Zn$: C, 59.1; H, 4.6; Zn, 13.4. Found: C, 59.3; H, 4.8; Zn, 13.6).

These intensely colored neutral metal complexes are very soluble in organic solvents such as ether, benzene, carbon tetrachloride, cyclohexanone and the monohydric alcohols. Increasing the chain length of the R group of III markedly increases the solubility of the complexes in saturated hydrocarbon solvents even of low molecular weight. Thus V (R = n-C_6H_{13}, Me = Fe, $m = 0$. Calcd. for $C_{34}H_{42}N_8Fe$: C, 66.0; H, 6.8; N, 18.1; Fe, 18.1; Fe, 9.0. Found: C, 65.7; H, 6.9; N, 18.2; Fe, 9.2) is best obtained in dark green microcrystals, m.p. 186° from n-hexane. Its molecular weight is 618. Similarly V (R = n-C_4H_9, Me = Ni, $m = 0$. Calcd. for $C_{30}H_{34}N_8Ni$: C, 63.7; H, 6.1; N, 19.8; Ni, 10.4. Found: C, 63.6; H, 6.2; N, 19.7; Ni, 10.5) is obtained in red needles m.p. 249–250° from cyclohexane.

Treatment of the neutral complexes V with acids leads to re-formation of the complex salts IV. Distribution of chelated metal between water and water-immiscible solvents thus depends on hydrogen ion concentration—a property of potential significance in biology (distribution of metal between aqueous media and lipids) metallurgy (extraction of metals from ores) and analytical chemistry.

Stability constant determinations show that both the salts IV and the neutral complexes V are very stable. Alcoholic solutions of the chelating agents I can extract transition metals with ease from their EDTA complexes. Some of the neutral complexes V can be sublimed *in vacuo*.

We have prepared similar type neutral complexes from N-heterocyclic hydrazones of simple aldehydes and ketones by removal with alkali of protons from the complex salts they give with transition metal salts when coördinating as bidentates. However, these are not so stable as the tridentate complexes. The osazones II form much more stable neutral complexes, especially with metals like palladium(II) which favor a square planar arrangement.

The molecules of all these multidentate chelating agents possess an acidic hydrogen atom attached to the nitrogen atom of each hydrazine residue proxi-

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