normal Claisen rearrangement" products such as IV, is indeed reversible, but that in the equilibrium between these phenols the latter type of isomer IV is heavily favored.

Experimental Section[8]

γ-Ethylallyl p-tolyl ether (Ib) was prepared from 1-chloro-2-pentene[9] and p-cresol by the method of Lauer[10] in 60% yield: bp 80–84° (2 mm), $n^{23}D$ 1.5118, strong infrared absorption at 970 cm^{-1}.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.89; H, 9.16. Found: C, 81.93; H, 9.04.

Thermolysis of Ib to a Mixture of o-(α-Ethylallyl)-p-cresol (IIb) and o-(α,γ-Dimethylallyl)-p-cresol (IVb).—Samples of Ib were sealed in Pyrex tubes, after degassing by freezing and melting repeatedly at *ca.* 0.1 mm, and the tubes were heated in an oven at temperatures which were maintained constant within <±2°. The rearrangement was followed by direct vpc and infrared analysis of the reaction mixtures. (Absorption at 915 cm^{-1} was characteristic of the terminal vinyl out-of-plane bending of IIb and, at 978 cm^{-1}, of the *trans* configuration about the internal double bond of IVb.) A sample heated for 23 hr at 160° showed no phenolic product. After 64 hr at 175°, *ca.* 90% of the starting material was unchanged; the product was almost pure IIb. After 303 hr at 175°, only a trace of starting material remained; the product was a mixture of IIb (major component) and IVb (minor component); the vpc was not well resolved on this sample. A sample heated for 24 hr at 200° was converted to IIb (*ca.* 40%) and IX (*ca.* 60%). The product mixture from the 200° thermolysis, which had a very slight brown tint, was analyzed directly.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.89; H, 9.16. Found: C, 81.66; H, 8.98.

Authentic IIb was obtained from Ib by the boron trichloride catalyzed rearrangement procedure which has been shown to give only the normal Claisen product from the ^{14}C-labeled crotyl homolog of Ib.[6] The crude product contained no IVb (vpc and infrared analysis), but some p-cresol, from cleavage of the phenolic ether (Ib); this was removed by preparative-scale vpc. The pure material showed strong infrared absorption at 915 cm^{-1} and no significant absorption at 978 cm^{-1}.

The methyl ether of IIb was prepared in the usual way,[6] and purified by preparative-scale vpc. Its nmr spectrum showed the following proton resonance absorptions: multiplet at τ 3.2 (3 H), multiplet at τ 4.1 (1 H), doublet at τ 5.1 (2 H), singlet at τ 6.3 (3 H), multiplet at τ 6.5 (1 H), singlet at τ 7.7 (3 H), quintet at τ 8.3 (2 H), and triplet at τ 9.1 (3 H).

Authentic IVb was synthesized from p-cresol and 4-chloro-2-pentene by the C-alkylation technique of Kornblum.[7] The crude reaction mixture was extracted with Claisen's alkali to separate the C-alkylation products from O-alkylation products. Work-up of the Claisen alkali-soluble fraction gave IVb in 50% yield: bp 82° (0.5 mm), showing only one vpc peak; strong infrared absorption appeared at 978 cm^{-1} and a very small absorption at 915 cm^{-1}.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.89; H, 9.16. Found: C, 81.83; H, 9.07.

The methyl ether of IVb was prepared as was that of IIb. The product (97% pure according to vpc) showed a strong infrared absorption at 975 cm^{-1} and a very weak absorption at 917 cm^{-1}. Its nmr spectrum exhibited the following proton resonance absorptions: multiplet at τ 3.3 (3 H), multiplet at τ 4.5 (2 H), multiplet at τ 6.2 (1 H), singlet at τ 6.3 (3 H), singlet at τ 7.8 (3 H), doublet at τ 8.3 (3 H), and doublet at τ 8.8 (3 H).

Rearrangement of IVb to IIb.—Samples (0.5, 0.5, and 0.1 g) of IVb in N,N-diethylaniline (1.0, 1.0, and 2.0 g) were degassed, sealed in Pyrex tubes, and heated at 200° for 24 and 48 hr and at

185° for 111 hr, respectively. Vpc analyses of the three reaction mixtures (after removal of the amine solvent as described below) were virtually identical, showing a single peak with a retention time corresponding to the starting material IVb and a small shoulder (estimated at *ca.* 3–5% of the large peak) at the retention time corresponding to IIb. Further vapor phase chromatography on the preparative scale gave a sample with increased concentration (*ca.* 50%) and better separation of the shoulder component. This sample showed significant infrared absorption at 915 cm^{-1}, characteristic of IIb.

A larger sample of IVb (6.5 g) was heated in N,N-diethylaniline (13 g) at 200° for 24 hr. The amine solvent was removed by aqueous hydrochloric acid extraction from a pentane solution of the crude reaction mixture. After further washing and drying of the pentane solution, the phenols were converted to their methyl ethers as before.[6]

Preparative-scale vpc provided almost complete separation of the methyl ether of IIb from the methyl ether of IVb, the major component. The analytical vapor phase chromatogram of the minor component showed one main peak with the same retention time as that of authentic IIb ether; the nmr and infrared spectra of the minor component were identical with those of authentic IIb ether.

Equilibration of IIb and IVb.—Thermolyses of separate samples (0.15 g) of authentic IIb and IVb in N,N-diethylaniline (0.3 g) were carried out at 200° for 9 days. Vpc analysis showed similar proportions of IIb (*ca.* 4%) and IVb (*ca.* 96%) in the two reaction mixtures.

The Identity of the Acetone–Urea Condensation Product

Takeshi Inoi, Takehiko Okamoto, and Yumiko Koizumi

The Central Research Laboratories, Chisso Corporation, Kamariya, Kanazawa-ku, Yokohama, Japan

The reaction of acetone with urea in the presence of mineral acid was investigated by Weinschenk,[1] who obtained a complex compound which melted with decomposition at 265–268°. This has been given the name "Triacetonediurea." As a possible structure for this presumed compound, to which he assigned the empirical formula $C_{11}H_{20}N_4O_2$, he considered the chain structure I, because alkaline or acid hydrolysis gave acetone, ammonia, and carbon dioxide as the products he could identify.
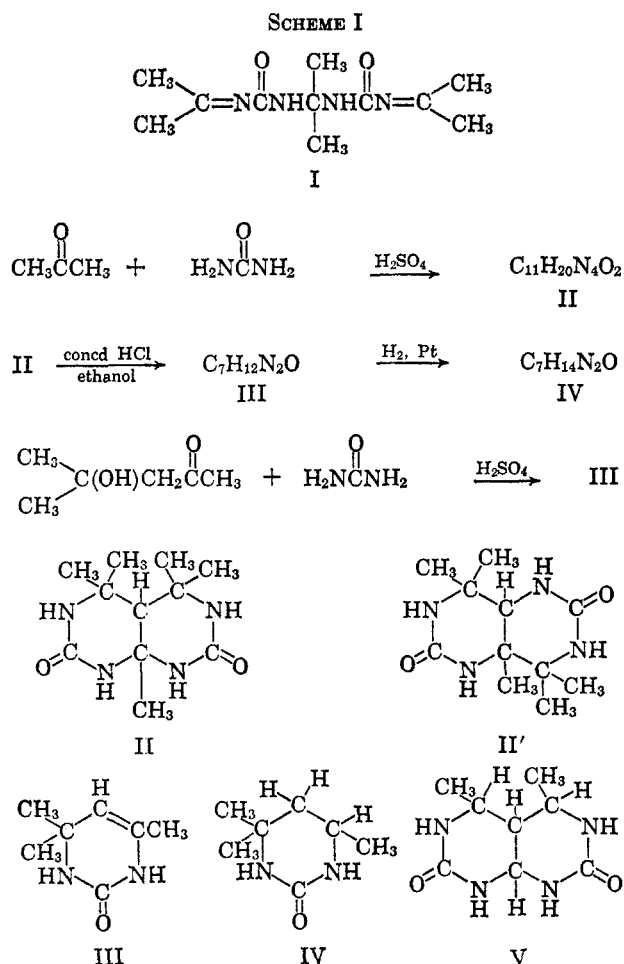
In 1951, another suggested structure, 4,4'-(2,2-dimethyltrimethylene)bis(4-methyl-2-uretidinone), was proposed in a patent reference[2,3] on the basis of the elementary analysis only.

In the present investigation, the structure of the acetone–urea condensation product has been re-examined. The product was obtained from the reaction of acetone with urea in the presence of sulfuric acid followed by basification of the reaction product. Recrystallization of this free base from water gave a hydrated crystalline solid which could be readily dehydrated by heating, mp 260–262° dec. The elementary analysis and molecular weight determination corresponded to a substance having an empirical formula of $C_{11}H_{20}N_4O_2$ (II). This showed no absorption

(8) Beckman IR-5A and Varian A-60 spectrometers were used in infrared and nmr measurements. Beckman GC-2A and Wilkens A-600 (Hi-Fi) and A-700 (Autoprep) instruments were used for vpc analyses and separations. The stationary-phase material most generally used was silicone gum rubber (SE-30); Carbowax (20M) and ethylene glycol succinate were used in some cases. Microanalyses were done by Alfred Bernhardt Microanalytisches Laboratorium, Mülheim, Germany.

(9) W. G. Young, F. F. Caserio, Jr., and D. D. Brandon, Jr., *J. Am. Chem. Soc.*, **82**, 6163 (1960).

(10) W. M. Lauer, G. A. Doldouras, R. E. Hileman, and R. Liepens, *J. Org. Chem.*, **26**, 4785 (1961).

(1) A. Weinschenk, *Ber.*, **34**, 2185 (1901).

(2) M. T. Harvey, U. S. Patent 2,592,565 (1952); *Chem. Abstr.*, **47**, 601a (1953).

(3) It will be noted that the chlorinated acetone–urea condensation product has the formula approximately $C_{11}H_{16}N_4O_2Cl_4$; see M. Kokorudz, U. S. Patent 3,158,436 (1964).

SCHEME I

$$CH_3\text{-}C\text{=}NCNHCNHCN\text{=}C(CH_3)_2$$

(with O, CH_3, O, CH_3 substituents)

I

$$CH_3\overset{O}{C}CH_3 + H_2N\overset{O}{C}NH_2 \xrightarrow{H_2SO_4} C_{11}H_{20}N_4O_2$$

II

$$II \xrightarrow[\text{ethanol}]{\text{concd HCl}} C_7H_{12}N_2O \xrightarrow{H_2, Pt} C_7H_{14}N_2O$$

III   IV

$$(CH_3)_2C(OH)CH_2\overset{O}{C}CH_3 + H_2N\overset{O}{C}NH_2 \xrightarrow{H_2SO_4} III$$

II   II'

III   IV   V

in the ultraviolet region. The infrared spectrum showed the patterns of an amide group,[4] the amide I band was found at 1662 cm^{-1}, but the spectrum lacked the amide II band in the 1570–1515-cm^{-1} region, which suggests that the cyclic amide structure may be indicated.

Repeated degradation reactions on II using aqueous alkaline hydrolysis gave acetone, ammonia, and carbon dioxide as Weinschenk mentioned, and hence gave little structural information. Treatment with concentrated hydrochloric acid in ethanol solution gave a colorless solid with the formula $C_7H_{12}N_2O$ (III), identical in every respect with the product prepared from diacetone alcohol and urea.[5] The ultraviolet spectrum of this hydrolyzed product, III, with one maximum at 246 mμ, suggested the formation of an unsaturated bond. The infrared absorption band at 835 cm^{-1} (CH=C) was also found. Catalytic hydrogenation of III gave a saturated compound IV, which had no maximum at 210–300 mμ and no absorption band at 835 cm^{-1}. From these findings it appeared that III is 2-oxo-4,4,6-trimethyl-1,2,3,4-tetrahydropyrimidine, in which 2 moles of acetone and 1 mole of urea are involved.

Thus, the structure of acetone–urea condensation product could be either 2,7-dioxo-4,4,5,5,8a-penta-methyldecahydropyrimido[4,5-d]pyrimidine (II) or the

(4) J. L. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley Sons, Inc., New York, N. Y. 1958, p 205.

(5) The patent literature [M. T. Harvey, U. S. Patent 2,782,197 (1957)] on the production of keto pyrimidines, describes a condensation product obtained by the reaction of diacetone alcohol and urea, for which the structure, 2-oxo-4,4,6-trimethyl-2,3,4,5-tetrahydropyrimidine, has been suggested. No evidence is given other than analytical values.

isomer II'. That the structure is correctly represented by II rather than by the alternative structure, II', was secured by its nmr spectrum. It showed three bands clearly with τ values 2.52 (singlet), 7.60 (singlet), 8.44 (singlet); the areas of these bands are in the ratio 4:4:12. They may be assigned, respectively, to the four >NH, one methyl and one hydrogen, and two equivalent *gem*-dimethyl hydrogen atoms but cannot be interpreted in terms of II'. It seems that the signal of the 4a proton should appear further upfield. However there was available an excellent model for comparison, 2,7-dioxo-4,5-dimethyldecahydropyrimido-[4,5-d]pyrimidine (V), prepared by condensation of 2-oxo-4-methyl-6-ureidohexahydropyrimidine with ac-etaldehyde as described by Zigeuner.[6] In this compound the resonance of the 4a proton was assigned to a multiplet at τ 7.60, interpreted by Dr. T. Ushioda of these laboratories. In the decahydropyrimido-[4,5-d]pyrimidine series, then the 4a proton should generally be assigned at τ 7.60.

The structure of the acetone–urea condensation product, "Triacetonediurea," was therefore established.

Experimental Section

Melting points are uncorrected. The ultraviolet spectra were recorded on a Hitachi EPS-3 spectrometer. The infrared spectra were taken with a JASCO IR-S spectrometer. The nmr spectra were obtained on a Varian A-60 instrument in trifluoroacetic acid, using tetramethylsilane as internal standard; the chemical shift are expressed in τ units. Assignment of protons in an area was based on correct integral information from the nmr spectra.

2,7-Dioxo-4,4,5,5,8a-pentamethyldecahydropyrimido[4,5-d]-pyrimidine ("Triacetonediurea") (II).—To finely powdered urea (60 g, 1.0 mole) suspended in 200 ml of acetone was added 100 g of sulfuric acid at such a rate that the temperature did not rise above 50°. When the exothermic reaction subsided the resultant mixture was stirred for 10 hr at a temperature of 60°, and allowed to stand overnight at room temperature. The precipitated sulfuric acid salt was removed by filtration and washed with cold methanol. After washing, the product was suspended in 400 ml of ice water and neutralized with 15% sodium hydroxide solution. The white solid product was filtered, washed with cold methanol, and dried under vacuum at 80° giving 87.6 g (73%) of the free base, mp 252–258° dec. An analytical sample was prepared by recrystallization from methanol and exhibited mp 260–262° dec; ν_{max}^{KBr} 3340, 3250, 3100, 2970, 1662, 1476, 1450, 1340, 1252, 1203, 1118, 1089, 1010, 820, 762, 733, and 589 cm^{-1}; nmr spectrum, singlet at τ 2.52 (>NH), singlet at 7.60 (4a proton and 8a methyl protons), and singlet at 8.44 (4- and 5-*gem*-dimethyl protons).

Anal. Calcd for $C_{11}H_{20}N_4O_2$: C, 55.0; H, 8.4; N, 23.3. Found: C, 54.8; H, 8.3; N, 23.5; mol wt (cryoscopic in water), 245.

The sulfuric acid salt was recrystallized from ethanol, mp 171–172° dec.

Anal. Calcd for $C_{11}H_{20}N_4O_2\cdot H_2SO_4$: C, 39.0; H, 6.5; N, 16.5. Found: C, 38.9; H, 6.6; N, 16.1.

2-Oxo-4,4,6-trimethyl-1,2,3,4-tetrahydropyrimidine (III). Hydrolysis of II.—A solution of II (1.20 g, 5 mmoles) in a mixture of concentrated hydrochloric acid (1.2 ml) and ethanol (12 ml) was heated under reflux for 8 hr. Most of the solvent was then removed and the residue was neutralized with 10% sodium hydroxide solution. The solid which formed was filtered off and then recrystallized from methanol, giving 0.17 g (24%) of product: mp 284–286° dec; λ_{max}^{pH5} 246 mμ (ϵ 1906); ν_{max}^{KBr} 3250, 3210, 2985, 1674, 1489, 1450, 1360, 1266, 1221, 1170, 835 (CH=C), 769, 700, 624 cm^{-1}.

Anal. Calcd for $C_7H_{12}N_2O$: C, 60.0; H, 8.6; N, 20.0. Found: C, 59.7; H, 8.6; N, 20.3; mol wt (cryoscopic in water), 137.

(6) G. Zigeuner, E. A. Gardziella, and G. Bach, *Monatsh.*, 92, 31 (1961). A suggested structure, 2,7-dioxo-4,5-dimethyldecahydropyrimido[4,5-d]-pyrimidine, for this compound is given in this report.

From Diacetone Alcohol.—To finely powdered urea (12.0 g, 0.2 mole) suspended in 29.0 g (0.25 mole) of diacetone alcohol was added 15.0 g of sulfuric acid at such a rate that the temperature did not rise above 40°. The resultant mixture was stirred for 12 hr at a temperature of 40°, diluted with 50 ml of water, and then neutralized with 15% sodium hydroxide solution. The crystalline precipitate was filtered, washed with cold water, and recrystallized from methanol giving 18.5 g (66%) of product, mp 284–286° dec. The infrared spectrum was identical with that of the compound prepared above.

Anal. Found: C, 59.9; H, 8.7; N, 20.4.

2-Oxo-4,4,6-trimethylhexahydropyrimidine (IV). Hydrogenation of III.—A suspension of 140 mg of platinum oxide in 1.40 g (10 mmole) of III and 30 ml of acetic acid was hydrogenated at atmospheric pressure for 2 hr to give a hydrogen uptake equivalent to 9.6 mmoles. After removal of the catalyst and acetic acid, the remaining residue was neutralized with 10% sodium hydroxide solution yielding 1.28 g of crude solid product. It was recrystallized from ethanol–ether to give 1.08 g (76%) of IV: mp 256–258°; ν_{max}^{KBr} 3250, 3110, 2920, 1660, 1490, 1460, 1366, 1339, 1260, 1238, 1198, 1143, 760, 690, and 630 cm^{-1}.

Anal. Calcd for $C_7H_{14}N_2O$: C, 59.1; H, 9.9; N, 19.7. Found: C, 59.3; H, 9.5; N, 20.1.

2,7-Dioxo-4,5-dimethyldecahydropyrimido[4,5-*d*]pyrimidine (V).[6]—The method described by Zigeuner was utilized in the preparation of this compound: mp 279–280° dec; nmr spectrum broad at τ 2.50 (>NH), singlet at 4.61 (8a proton), multiplet at 6.00 (4 and 5 protons), multiplet at 7.60 (4a proton), and quartet at 8.40 (4- and 5-methyl protons); the area ratios of these peaks were 4:1:2:1:6.

Displacement Reactions. XI.
The Oxibase Parameters of Thio Anions[1]

ROBERT EARL DAVIS,[2] HISHAM NAKSHBENDI,
AND ATSUYOSHI OHNO

*Department of Chemistry, Purdue University,
West Lafayette, Indiana*

Thio anions, RS$^-$, are some of the best nucleophiles for S_N2 displacement reactions;[3–5] yet it is remarkable that accurate kinetic parameters are not available for many thio anions. It is the purpose of this note to communicate the oxibase scale[6] parameters[7] of numerous thio anions in water at 25° with numerous substrates. The parameters are also related to the basic properties of the ions.

The rate constants have been determined by measuring the change in the ultraviolet spectrum of the reaction mixture. Dilute deoxygenated solutions (10^{-4}– 10^{-2} M) of the reactants in dilute buffer solutions (0.1 M maximum) were allowed to react in sealed quartz ultraviolet cells in a thermostated compartment.

(1) Paper X: R. E. Davis, R. Nehring, S. Molnar, and L. A. Suba, *Tetrahedron Letters*, in press.

(2) Alfred P. Sloan Fellow, 1962–1966.

(3) C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, **75**, 141 (1953).

(4) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(5) E. R. Thornton, "Solvolysis Mechanisms," The Ronald Press Co., New York, N. Y., 1964.

(6) J. O. Edwards, *J. Am. Chem. Soc.*, **76**, 1540 (1954); **78**, 1819 (1956). J. O. Edwards and R. G. Pearson, *ibid.*, **84**, 16 (1962).

(7) R. E. Davis, "Survey of Progress in Chemistry," Vol. 2, A. Scott, Ed., Academic Press Inc., New York, N. Y., 1964, pp 189–238.

In some cases a stopper flow mixer was used if the half-times were <60 sec but >5 μsec.

The data at 25° in water are presented in Table I. The data represent about 400 kinetic experiments (temperatures 0–35°). The products of each reaction were analyzed.

TABLE I

KINETIC RATE CONSTANTS AT INFINITE DILUTION IN WATER AT 25.00°[a]

Anion[b]	Substrate[c]	pH range[d]	k_2 M^{-1} sec^{-1e}
Et$_2$NCS$_2^-$	β-Propiolactone[f]	6.7–7.5	0.304 ± 0.009
	Iodoacetate	5.9–8.2	2.20 × 10^{-2}
	Bromoacetate	5.9–8.2	5.38 × 10^{-3}
EtSCS$_2^-$	β-Propiolactone[f]	7.0–7.6	6.70 ± 0.04 × 10^{-2}
EtOCS$_2^-$	β-Propiolactone[f]	7.0–9.2	0.112 ± 0.003
	Iodoacetate	5.0–6.9	1.66 ± 0.05 × 10^{-1}
CH$_3$CS$_2^-$	β-Propiolactone[f,g]	7.3–11.9	4.53 ± 0.10 × 10^{-2}
CS$_3^{2-}$	β-Propiolactone[f]	9.2–11.9	0.42 ± 0.03

[a] The α and β values for each substrate and all kinetic measurements with the standard deviations are reported in ref 6, 7, and 13. [b] Anions as the sodium salts. Concentrations varied from 1.1 to 11.9 × 10^{-4} M. [c] Substrates as sodium salts. Concentrations varied from 1.7 to 15.1 × 10^{-3} M for the acetates and from 10^{-2} to 2 × 10^{-1} M for β-propiolactone. [d] pH range of the dilute buffer solutions. The rates were independent of the pH. [e] Second-order rate constant with the σ. [f] Kinetic rates were obtained only ionic strengths of μ = 0.01–0.10. Since the k_2 values are nearly independent of μ; no extrapolation μ = 0 was made. [g] An E value of 2.1 can be computed using the α and β value of musturd and the rate data of Ogston [A. G. Ogston, E. R. Holiday, J. St. L. Philpot, and L. A. Stocken, *Trans. Faraday Soc.*, **44**, 45 (1948)].

Using the oxibase scale[6,7]

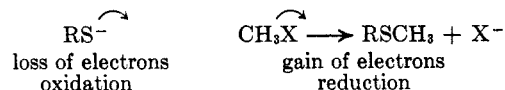$$\frac{\log k/k_0}{E} = \alpha + \beta \left(\frac{H}{E}\right)$$

where

$$X^- + AY \xrightarrow{k} AX + Y^-$$

$$H_2O + AY \xrightarrow{k_0} AOH + Y^- + H^+$$
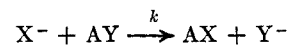
and

$$2X^- = X_2 + 2e^-, E = \epsilon_{X^-}^0 + 2.60 \text{ v}$$
$$H^+ + X^- = HX, H = pK_{aX^-} + 1.74$$

and the α and β values for each substrate,[6,7] the E values were computed by a multiple regression technique[8] since the pK_a values are available in the literature[7] to compute H ($= pK_a + 1.74$).[6] The oxibase scale values are listed in Table II and compared with the values of other thio anions.

The thio anions are excellent nucleophiles on carbon because they are very easily oxidized.

$$\overset{\frown}{RS^-} \qquad CH_3\overset{\frown}{X} \longrightarrow RSCH_3 + X^-$$

loss of electrons   gain of electrons
oxidation   reduction

Calculations have been made of the properties of the ions using an Extended[9] Huckel Method[10] but using all the 1s–3p electrons in an SCF program.[10] However, even the simple π-LCAO-MO-SCF method on the

(8) Wald Method with Confidence Bands. Program in Fortran IV is available upon request. We assume errors in all variables: k, k_0, α, β, E, and H.

(9) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(10) The EHM–SCF program is similar to that reported by E. B. Moore, Jr., *Inorg. Chem.*, **4**, 1084 (1965).