the estimated standard deviations are less than 0.02 A, there appear to be just three cases: (1) N-bonded covalent compounds, in which C–N is 1.17–1.22 A and C–S is 1.56 A; (2) one S-bonded covalent compound in which C–N is 1.21 A and C–S is 1.61 A; and (3) the metal complexes and salts, which include both N-bonded and nonbonded thiocyanate groups, in which C–N is 1.13–1.17 A and C–S is 1.61–1.69 A. It seems best to defer any attempt to explain these bond distances until more accurate values are available.

The general arrangement of the ions and the hydrogen-bond network are shown in Figure 2. The nitrogen atom, N(6), of the uncoordinated thiocyanate ion accepts two hydrogen bonds, with N···N distances of 3.10 A, from N(2) and N(4) of two different cations. The sulfur atom, S(2), of the uncoordinated thiocyanate ion accepts a hydrogen bond, with a N···S distance of 3.49 A, from N(2), while the sulfur atom, S(1), of the coordinated thiocyanate ion accepts a hydrogen bond from N(4) with a N···S distance of 3.51 A.

Acknowledgments. Our sincere thanks are due to Professor F. Basolo of Northwestern University for furnishing us with the crystal sample. We are also thankful to the National Science Foundation for their financial support of this research and to the Computer Center of the University of Washington for giving us the free computer time for calculations. One of us (P. C. J.) is indebted to the Kurukshetra University, Kurukshetra, India, for a grant of leave of absence.

Stereochemically Nonrigid Organometallic Molecules. VIII. Further Studies of σ-Cyclopentadienylmetal Compounds[1]

F. A. Cotton, A. Musco, and G. Yagupsky

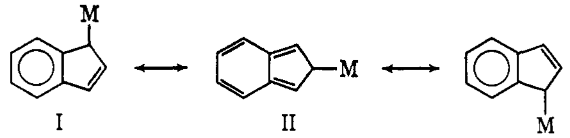
Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received June 23, 1967*

Abstract: The temperature dependence of the proton nmr spectrum of $(\pi\text{-}C_5H_5)Cr(NO)_2(\sigma\text{-}C_5H_5)$ has been studied down to −110°. The pattern of change is very similar to that previously observed in the isoelectronic $(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_5H_5)$. It is concluded that the same mechanism (presumably a series of 1,2 shifts) is predominant for the intramolecular rearrangement ("ring whizzing") in both compounds, though the rate is greater in the chromium case. $(\pi\text{-}C_5H_5)Fe(CO)_2$(1-indenyl) has been prepared and found to be a rigid (nonfluxional) molecule up to 70°. It is shown that this would be expected if rapid 1,2 shifts, but not 1,3 shifts, are operative in the $\sigma\text{-}C_5H_5$ cases. By decoupling and deuteration experiments, it is shown that in the ABX spectrum of $(\pi\text{-}C_5H_5)Fe(CO)_2$(1-indenyl), which closely resembles the low-temperature A_2B_2X spectrum of $(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_5H_5)$, $J_{BX} \ll J_{AX} \approx 2.2$ cps, and the A proton has a lower τ value than the B proton. These results support the arguments previously used to deduce the 1,2 shift mechanism for $(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_5H_5)$.

In an earlier paper in this series,[2] an investigation of the molecule $(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_5H_5)$ was reported. A combination of X-ray work and study of the variation of the proton nmr spectrum as a function of temperature lead to the following main conclusions: (1) the molecule does have the kind of instantaneous structure implied by the formula $(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_5H_5)$; (2) the intramolecular rearrangement process which causes the time-average equivalence of the five protons of the $\sigma\text{-}C_5H_5$ group at room temperature is a sequence of 1,2 shifts, probably having a polar metal–olefin complex as a transition state.

With these results in view, a number of further studies readily suggest themselves. Among these are (a) studies of homologous and/or isoelectronic molecules, such as $(\pi\text{-}C_5H_5)Cr(NO)_2(\sigma\text{-}C_5H_5)$, and (b) studies of some σ-indenylmetal compounds. The study of σ-indenyl compounds was expected to afford useful information regarding the validity of the previously proposed 1,2-shift mechanism (as opposed to a 1,3-shift mechanism) for $(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_5H_5)$ in two ways.

First, if the only low-energy path for rearrangement of $(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_5H_5)$ is indeed the one involving 1,2 shifts, then $(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma$-indenyl) should not exhibit fluxional behavior. This prediction is based on the fact that rearrangement by a sequence of 1,2 shifts would have to follow the course shown in eq 1. That is, in order to interconvert the equivalent structures I and III, and thus give the molecule a time-average plane of symmetry perpendicular to the molecular plane, it would be necessary to pass through structure II. However, on the basis of Hückel LCAO-MO calculations,[3,4] the type of π-electron distribution in II is about



I II III (1)

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[1] (a) Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. (b) Previous paper in this series, part VII: W. K. Bratton, F. A. Cotton, A. Davison, A. Musco, and J. W. Faller, *Proc. Natl. Acad. Sci. U. S.*, **58**, 1324 (1967).

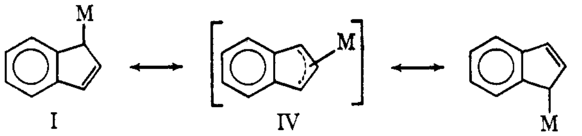
[2] M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Am. Chem. Soc.*, **88**, 4371 (1966).

[3] The delocalization energies of I and II were taken to be equal to those of styrene and *o*-xylylene, respectively, and the calculated values for the latter molecules were obtained from a published tabulation.[4] Even if the absolute values for the individual systems may be somewhat uncertain, the difference should be rather reliable because of the cancellation of systematic errors in the two Hückel calculations.

[4] C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations," W. H. Freeman & Co., San Francisco, Calif., 1965. Calculations with neglect of overlap ($S = 0$) yield a difference of 9.4 kcal/mole, while calculations with $S = 0.25$ yield a difference of 8.6 kcal/mole.

9 kcal/mole less stable than that in I and III. Consequently, the over-all process of passing from I to III, *via* II, cannot be expected to attain a sufficient rate to give an averaged spectrum at room temperature.

On the other hand, if the previous conclusion[2] of a 1,2 shift is, for some reason, incorrect, and a 1,3 shift with a π-allyl-like transition state is, instead, the correct pathway, then the indenyl system should be capable of rapid rearrangement, since the formation of the π-allyl complex IV is not significantly inhibited by the presence of the fused benzene ring as indicated in eq 2.


I IV III (2)

The second way in which nmr data on (π-C_5H_5)Fe(CO)$_2$(1-indenyl) might be useful in corroborating (or, perhaps, disproving) the suggested 1,2-shift mechanism in (π-C_5H_5)Fe(CO)$_2$(σ-C_5H_5) depends on the indenyl compound being rigid, as, in fact, it is found to be. Then, a study of its nmr spectrum, employing spin decoupling and suitably deuterated molecules, provides an opportunity to verify the earlier assignment[3] of the A_2B_2X spectrum observed at −80° in (π-C_5H_5)Fe(CO)$_2$(σ-C_5H_5).

Experimental Section

Preparation of (π-C_5H_5)Cr(NO)$_2$(σ-C_5H_5). The compound (π-C_5H_5)Cr(NO)$_2$Cl was prepared by the method of King.[5] A 2-g (0.01 mole) portion was treated with an equimolar quantity (2.7 g in 50 ml of dry, deoxygenated benzene) of C_5H_5Tl,[6] which had been previously purified by sublimation. The mixture was stirred for 2 hr at room temperature until the color of the suspension turned brown. After removal of the solvent (using a water suction pump), the residue was extracted with 250 ml of degassed petroleum ether. The extracts were concentrated and passed through an alumina chromatography column. Only one band was developed by using petroleum ether as an eluent. The solvent was evaporated, yielding a brown oil. Brown crystals were obtained by recrystallization from petroleum ether at −70°, yield 400 mg, 16% based on (π-C_5H_5)Cr(NO)$_2$Cl. The product was identified as the compound previously prepared in a different way[7] by comparison of melting point and infrared and nmr spectra.

Preparation of (π-C_5H_5)Fe(CO)$_2$(1-indenyl). All the operations were carried out under nitrogen. Indenylsodium[8] (66 mmoles in 150 ml of THF) was treated with an equimolar quantity (20 g) of (π-C_5H_5)Fe(CO)$_2$I, purchased from Alfa Inorganics, Inc. The solution was stirred at 25° for 5 hr. The solvent was then removed using a water suction pump. The residue was extracted with benzene (100 ml) and the solution filtered through a coarse sintered-glass disk. The filtrate was concentrated using the water pump and then put on a 5 × 60 cm alumina column. A 1:3 mixture of benzene and petroleum ether was used as the eluent. Three bands were developed and eluted in the following order: (1) orange, (2) brown, (3) red-brown. The orange band (1) was rechromatographed using petroleum ether as eluent until it appeared to be entirely separated from the material in band 2. Upon removing the solvent, an oily, sticky residue was obtained. This was dried on a vacuum pump for 1 hr. After standing for several hours at 25° this oil solidified. It was then recrystallized from petroleum ether, giving red crystals, mp 62–64°, yield 4 g; 20% based on (π-C_5H_5)Fe(CO)$_2$I. The infrared spectrum has two strong CO stretching frequencies at 2010 and 1955 cm^{-1} (±5 cm^{-1}) in heptane solution.

Anal. Calcd for $C_{16}H_{12}FeO_2$: C, 65.78; H, 4.14. Found: C, 66.3; H, 4.22.

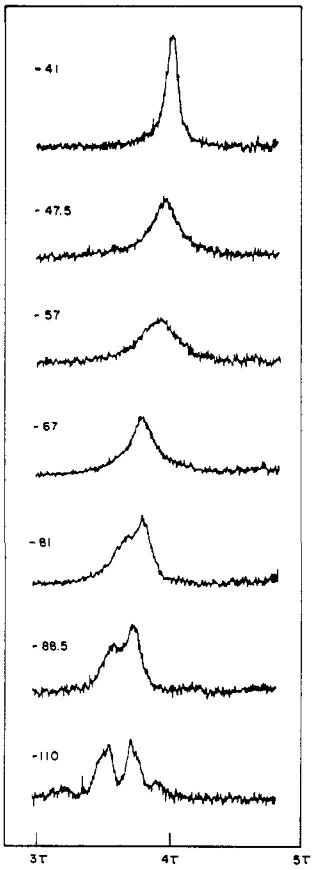


Figure 1. The behavior of a portion of the proton nmr spectrum of (π-C_5H_5)Cr(NO)$_2$(σ-C_5H_5) as a function of temperature in CS_2 solution. The top trace (at −41°) represents the partially broadened line due to the five protons of the σ-C_5H_5 ring. The traces at the lowest temperatures are due to the four vinyl protons of the σ-C_5H_5 ring.

The corresponding 1,3-dideuterio compound was prepared from 1,1,3-trideuterioindene, which was made by successively hydrolyzing lithium indenide in ether with D_2O, repreparing the lithium indenide, etc., through three cycles. The identity of the trideuterio compound[9] and the extent of deuteration were monitored by recording the nmr spectra.

Nmr Spectra. These were measured at 60 Mc using a Varian Associates A-60 nuclear magnetic resonance spectrometer equipped with a variable-temperature accessory. Temperatures were determined by measuring the peak separations for methanol and converting these data to temperatures using the shifts *vs.* temperature chart supplied by Varian Associates. Decoupling was done with a Varian V-6058A decoupler.

Results

π-Cyclopentadienylchromium Dinitrosyl σ-Cyclopentadiene. The main results on this compound are presented in Table I and Figure 1. In the room-temperature (+30°) spectrum of this compound the resonance due to the five σ-C_5H_5 protons is just as sharp as that of the π-C_5H_5 protons. This in itself is an indication that the fluxional process here is more rapid than that in (π-C_5H_5)Fe(CO)$_2$(σ-C_5H_5), the isoelectronic molecule previously studied,[2] since, for the iron compound at +30°, the σ-C_5H_5 resonance is about 1.5 times as broad as the π-C_5H_5 resonance. Consistent with this, we were unable to achieve the same degree of resolution in the low-temperature spectrum, even at −110°, for the chromium compound that was obtained at −80° for the iron compound. However, the general

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[5] R. B. King, "Organometallic Syntheses," Vol. 1, J. J. Eisch and R. B. King, Ed., Academic Press Inc., New York, N. Y., 1965, p 161.

[6] C. C. Hunt and J. R. Doyle, *Inorg. Nucl. Chem. Letters*, **2**, 283 (1966).

[7] T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

[8] Reference 5, p 74.

[9] G. Bergson, *Acta Chem. Scand.*, **18**, 2003 (1964).

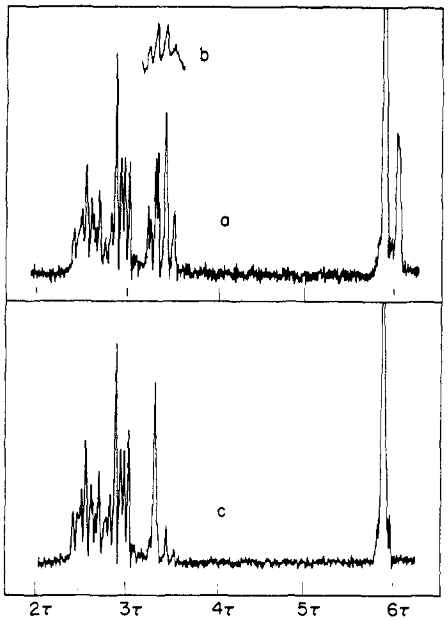

Figure 2. (a) The complete proton nmr spectrum of (π-C_5H_5)-$Fe(CO)_2$(1-indenyl) at 25° in $CDCl_3$. (b) The appearance of the A and B proton resonances of the iron compound with the X resonance decoupled. (c) The complete proton nmr spectrum of (π-C_5H_5)$Fe(CO)_2$(1,3-dideuterioindene) in $CDCl_3$.

trend in the temperature variation of the spectrum is qualitatively the same as for the iron compound, and there is no reason to doubt that the same mechanism is operative in both cases. In fact, in the present case, comparison of the observed spectra with computer-simulated spectra for various rate constants leads to a very satisfactory correlation.

Table I. Chemical Shifts in the Spectra of (π-C_5H_5)$Cr(NO)_2$(σ-C_5H_5) at Various Temperatures

Temp, °C	Peak positions, τ			
+30			4.04	5.13[a]
−41			4.04	5.13
−47.5			3.96	5.13
−57			3.93	5.13
−67		3.79		5.13
−110	3.50	3.72		5.13

[a] Peak due to the π-C_5H_5 protons.

In their study of (σ-C_5H_5)$CuP(C_2H_5)_3$, Whitesides and Fleming[10] calculated spectra for a range of pre-exchange lifetimes, τ, for fluxional (σ-C_5H_5)-M systems rearranging by 1,2 shifts, 1,3 shifts, and for a random mixture of both types of shift. In particular, for the case of 1,2 shifts, their spectra were computed for almost exactly the same chemical shift differences between the A, B, and X resonances which we observed in the low-temperature A_2B_2X spectrum of (π-C_5H_5)$Cr(NO)_2$-(σ-C_5H_5), and the appearance of this series of computer spectra matches almost exactly the spectra we have observed (compare Figure 1 of this paper with Figure 2 in the paper of Whitesides and Fleming). Therefore, just as in the case of (π-C_5H_5)$Fe(CO)_2$(σ-C_5H_5), provided we are correct in assuming that the low-field side of the A_2B_2 resonance centered at τ 3.61 receives a greater contribution from the A protons (those on the carbon atom α to the carbon atom attached to the metal atom) than from the B protons, the conclusion that the rearrangement process ("ring whizzing") proceeds by a series of 1,2 shifts follows rigorously from the experimental data.

With the help of the computed spectra of Whitesides and Fleming, it is possible to make some order of magnitude estimates of the rates, 1/τ, at various temperatures for the 1,2 shift. Thus at about −55° the rate must be around 10^3 sec^{-1} and around 10^2 at about −70° while at about −110° a rate of about 10 sec^{-1} can be estimated. By a very crude extrapolation, the rate at room temperature would appear to be around 10^6 sec^{-1}.

Indenyl Compound. The main experimental results for the indenyl compound, (π-C_5H_5)$Fe(CO)_2$(1-indenyl), are shown in Figure 2. According to the argument in the introductory section, if a 1,3 shift can occur readily in (π-C_5H_5)$Fe(CO)_2$(σ-C_5H_5), it would also be expected to occur here, thus making the indenyl compound a fluxional molecule. The effect would be to give time-average equivalence to the protons on carbon atoms 1 and 3. Thus an A_2X spectrum should be observed, in addition to the resonances of the aromatic protons. On the other hand, if the 1,2-shift mechanism provides the only important path for rearrangement of (π-C_5H_5)Fe-$(CO)_2$(σ-C_5H_5), then (π-C_5H_5)$Fe(CO)_2$(1-indenyl) should be a rigid or nonfluxional molecule, and therefore display an nmr spectrum consisting of an ABX pattern as well as complex absorption due to the aromatic protons.

It may be seen in Figure 2 that in fact the ABX pattern is observed. This spectrum persists without any detectable broadening up to 70°. The two doublets at τ 3.28 and 3.47 each of relative intensity 1 are due to the nonequivalent protons (A, B) on carbon atoms 2 and 3, while the peak of relative intensity 1 at τ 6.03 is due to the proton (X) on carbon atom 1. The complex absorption of total relative intensity 4 lying between τ 2.35 and 3.05 is due to the four aromatic protons.

It will be noted that the group of peaks due to the nonaromatic protons, the ABX set, is quite similar in the distribution of chemical shifts to the set of A_2B_2X peaks observed in the low-temperature spectra of (π-C_5H_5)$Fe(CO)_2$(σ-C_5H_5) and (π-C_5H_5)$Cr(NO)_2$-(σ-C_5H_5). Thus a detailed study of the ABX set was undertaken in order to establish the assignments of the A and B resonances. Since the indenyl molecule is nonfluxional at room temperature, this is relatively easy to do, whereas it has proved an impossibility in practice, though not in principle, to do so for the two fluxional molecules. It would then be considered fairly probable, although not rigorously certain, that the main conclusions reached for the ABX spectrum of the indenyl system would be applicable also to the A_2B_2X spectra of the σ-C_5H_5 systems at low temperature.

By a combination of a spin-decoupling experiment and study of the 1,3-dideuterio analog of (π-C_5H_5)Fe-$(CO)_2$(1-indenyl), the assignment of the ABX spectrum has been established unambiguously. It is seen in Figure 2a that of the two doublets due to the A and B protons, the components of the one at lower τ are each split (2.0–2.5 cps) into doublets. This splitting vanishes (Figure 2b) when the sample is irradiated at the resonance frequency of the X proton, thus confirming that the X proton is coupled to either the A *or* the B proton by 2.0–2.5 cps but is *not* resolvably coupled to the other one. The problem remaining, then, is whether $J_{AX} \gg$

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(10) G. M. Whitesides and J. S. Fleming, *J. Am. Chem. Soc.*, **89**, 2855 (1967).

J_{BX} or $J_{BX} \gg J_{AX}$. This question is unambiguously answered by the results of the deuteration experiment. It is seen that when the B proton (as well as the X proton) is replaced by deuterium, it is the upper doublet (at τ 3.47) which disappears, while the one centered at τ 3.28 collapses to a single line because of the loss of AB coupling. Thus it is clear that (1) the lower doublet is due mainly to the A proton, and (2) $J_{AX} \gg J_{BX}$. These are precisely the assumptions made in the study[2] of $(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2(\sigma\text{-C}_5\text{H}_5)$, thus leading to the conclusion that 1,2 shifts accounted for the fluxional ("ring-whizzing") behavior of the σ-C_5H_5 ring in that molecule.

It is interesting to note that according to the detailed analysis of the spectrum of indene by Elleman and Manatt[11] $|J_{AX}| \approx |J_{BX}| \approx 2$ cps though the two coupling constants differ in sign. Also, the A proton absorbs at a higher field than the B proton. It is thus evident that attachment of indene at the 1 position to the $(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2$ moiety, which may have considerable diamagnetic anisotropy, causes marked changes in both the spin–spin couplings (J_{BX} becoming very small, J_{AX} remaining of the same absolute magnitude) and in the relative chemical shifts. Manatt and Elleman, as quoted by Whitesides and Fleming,[10] have found for cyclopentadiene that $|J_{AX}| \approx |J_{BX}| \approx 1.3$ cps, whereas in the low-temperature spectrum of $(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2(\sigma\text{-C}_5\text{H}_5)$ it was concluded[2] that $|J_{AX}|$ remained in the range 1–2 cps while J_{BX} became very small. Thus, in this respect there is a clear parallel between the σ-C_5H_5 and 1-indenyl systems suggesting that the two have generally similar behavior.

Acknowledgment. It is a pleasure to thank Professor George Whitesides for useful advice and for information on his work in advance of publication.

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σ- and π-Bonding Effects in the Coordination of the Cyano Group

Keith F. Purcell[1]

Contribution from the Department of Chemistry, Wake Forest College,
Winston-Salem, North Carolina 27106. *Received April 7, 1967*

Abstract: The effect of CN^- π^*-orbital occupation on the CN force constant and bond strength is examined by LCAO–MO computations. In addition to emphasizing the opposing influences of CN σ stabilization and π destabilization when the cyano group coordinates "electron-rich" acids, the LCAO–MO results are examined in relation to nuclear quadrupole resonance data and the Lewis-base properties of the free and coordinated cyano group. The molecules considered are NCN^{2-}, OCN^-, and SCN^-, and results for these molecules are compared with those obtained earlier for CN^-, ClCN, BrCN, and ICN as well as CH_3CN, CH_3NC, and HCN.

In continuing our investigations into the effects of coordination on the cyano group, we wish to report the results of modified Hückel calculations for NCN^{2-}, OCN^-, and SCN^-. The ion N^- and atoms O and S are examples of back-bonding "acids" which are capable of donating electron density to the π-antibonding orbitals of the CN^- ligand. One goal of this approach is to study the relative importance of σ- and π-bonding changes over a series of related cyano molecules with regard to their effects[2] on the CN vibrational frequency and force constant.

The nitrile group is particularly interesting for study since the CN stretching frequency generally increases upon either carbon or nitrogen coordination. Earlier studies[3] have shown that kinematic coupling is only partly responsible for the observation. In fact, molecular orbital calculations show that the increase in F_{CN} is due, in general, to σ strengthening although electron polarization effects are evident. In the adducts considered previously, only primarily σ-bonding acids were considered and back-bonding was not sufficiently important to offset σ-bond strengthening and bring about a decrease in F_{CN} and ν_{CN}. Because of the great interest in back-bonding to the cyano group in some of its complexes, we now wish to report a similar examination of the factors mentioned above for highly electron-rich or back-bonding acids and compare them to the "σ-bonding" acids. Forthcoming reports will deal with the equally interesting NO and CO ligands.

Calculations

The LCAO–MO method used here is the same in every respect as that used previously. An earlier report[3a] can be consulted for a discussion of the parameterization in the molecular orbital calculations and the method of analysis in terms of Mulliken's population procedure.

Overlap integrals were calculated from Slater-type orbitals. Initial, neutral atom H_{ii}'s were taken as valence-state ionization potentials[4] and the H_{ij} approximated from the MWH formula[5,6] with $K = 1.75$. The initial secular determinant was solved; atom charges were calculated, the H_{ii}'s corrected by 2.0 ev/unit charge, the Slater exponents adjusted by Slater's rules, the overlap integrals recomputed; and the new secular determinant was solved, etc. The iteration was halted when successive cycles yielded changes in charge on each atom of less than 0.01. The final results have been analyzed in terms of orbital populations and overlap energies.[7]

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[3] (a) K. F. Purcell, *J. Am. Chem. Soc.*, **89**, 247 (1967); (b) K. F. Purcell and R. S. Drago, *ibid.*, **88**, 919 (1966).

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