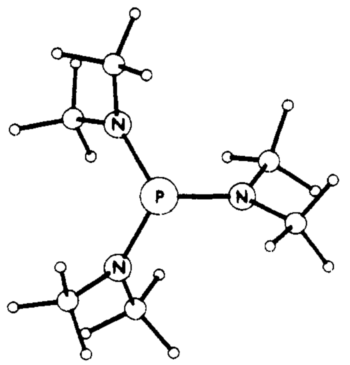

Figure 2. A projection of the optimized MNDO geometry (model E) of P(NMe$_2$)$_3$, viewed down the C_3 axis.

seen, irrespective of whether the nitrogen geometry is optimized or held planar, conformation E is predicted to be the most stable. The other models optimize into conformation E, with the dihedral angle about the P–N bonds (ϕ_{PN}) equal to ca. 61°, upon removal of the P–N torsional angle constraints. The MNDO geometry for model E is remarkably similar to that proposed by Vilkov et al.[7] in that ϕ_{PN} is computed to be 61° as compared with the 60° angle found by electron diffraction. Furthermore, the MNDO results support the conclusion of Vilkov et al. that the nitrogens in **1** are close to planar, although there is some deviation from planarity (the N–C bonds are calculated to be only 6° out of the trigonal planes containing each P–N bond). It should be noted that the nitrogen deformation is regular, and the C_3 propeller symmetry is preserved. A projection of this optimized conformation is depicted in Figure 2.[18] The calculated P–N bond length in the E conformation of **1** (**1E**), r_{PN} = 1.67 Å, is in good agreement with recent X-ray crystallographic measurements on the iron tricarbonyl adduct of **1** (r_{PN} = 1.67 Å)[13] and with the electron diffraction data for **1** (r_{PN} = 1.70 Å),[7] although the calculated NPN bond angle (106°) is somewhat larger than the electron diffraction value (96.5°).[7] The computed N–C and C–H bond lengths (1.45–1.46 and 1.1 Å, respectively) are in *exact* accord with the electron diffraction values.[7,19]

The MNDO results (Table I) predict that the C_{3v} conformation D proposed by Lappert et al.[9] is very unstable and can certainly be excluded as a candidate for the ground state of **1**. Similarly, conformation C is 14 kcal mol^{-1} less stable than E and can also be excluded. Conformation A is closest in energy to E, but the UPS of **1** is markedly different from that observed for a caged analogue constrained to model A geometry.[2] The C_s conformation B, which has been generally favored as the ground state of **1**[8,10,11] is calculated to be 3 kcal mol^{-1} less stable than E. Furthermore, the orbital ordering predicted by MNDO for this model (Table I) is

$$\text{out-of-phase } \pi_{PN} > \text{out-of-phase } \sigma_{NN} > \text{in-phase } \sigma_{NN} > \text{in-phase } \pi_{PN}$$

which is not in accord with the previous UPS assignments for this model based upon crude HMO/PMO arguments.[2,8,10] This orbital ordering is somewhat difficult to reconcile with the fact that *N*-alkyl substitution causes a substantially greater shift in UPS bands 1 and 4 than in UPS bands 2 and 3.[10]

If model E is indeed the lowest energy conformer for **1**, then none of the UPS data reported to date for **1** has been interpreted correctly. A revised interpretation of the UPS data based upon conformational model E would require that the second- and third-band components in the UPS correspond to ionization of the doubly degenerate lone-pair orbitals with a Jahn–Teller splitting of 0.84 eV (see experimental ionization energies in Table I). These two orbitals are predicted by MNDO to have near nodes at phosphorus. The first and fourth orbitals are predicted to have substantial phosphorus and nitrogen lone-pair character. If the experimental splitting of the second- and third-band components in the UPS of **1** is assumed to be due to Jahn–Teller distortion, the extrapolated MNDO ionization energies (Koopmans' theorem) would be 9.36 and 10.20 eV. Upon consideration of these values with the predicted first (9.18 eV) and fourth (11.33 eV) ionization energies for **1E**, we find that a rather close fit of the experimental ionization potentials and MNDO ionization energies is obtained with a nearly constant 1.5-eV correction. Such a revised UPS interpretation for **1** still must be viewed with caution, however, because the UPS of the caged compound P[N(Me)CH$_2$]$_3$CMe for which model A must apply does *not* contain resolved Jahn–Teller components[2] and a 0.84-eV Jahn–Teller distortion for **1** seems abnormally large for a nonbonding degenerate orbital.

In conclusion, it would appear that the previous UPS interpretations for **1** based upon HMO/PMO arguments may be in doubt, given that MNDO has proved to be remarkably reliable in predicting orbital ordering for the highest several occupied MO's for a variety of molecules.[14,16,17] The MNDO preferred geometry of **1** is in fact the C_3 model E originally proposed by Vilkov et al., although we believe that model B provides a better fit of the UPS data. In any case the MNDO calculations indicate with certainty that the energies of conformational models A, B, and E are very close.

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Registry No. **1**, 1608-26-0.

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[18] The direction of the nitrogen deformation is such that the *N*-methyl groups are moved slightly closer to the phosphorus lone pair; hence the primary lobe for the nitrogen lone-pair orbital subtends a dihedral angle of 119° with the phosphorus lone pair.

[19] The optimized geometries for any or all of the model conformations will be made available upon request.

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Comparison of Metal-Metal Bond Energies in the Chromium(II) and Copper(II) Acetate Dimers

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Binuclear complexes of the type M$_2$(OOCR)$_4$ (M = Cr,[1] Cu,[2] and other metals[3,4]) are well-known, and the nature of the metal–metal bond has been discussed, but so far the actual bond strengths have not been compared. Dissociation equilibria have been reported for the chromium(II) and copper(II) acetates, though not under the same conditions. In this note, we use the data to estimate the difference between the Cr–Cr and Cu–Cu bond energies.

The dissociation constant K_{DO}^{Cr} of the chromium complex in aqueous solution has been directly determined by Cannon

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and Gholami[5] as $\log K_{DO}^{Cr} = -4.4$ at 25 °C (I = 3.0M) (see eq 1).

$$Cr_2(OAc)_4(aq) \overset{K_{DO}^{Cr}}{\rightleftharpoons} 2Cr(OAc)_2(aq) \qquad (1)$$

Gerding[6] has studied copper(II) acetate equilibria with variation of copper concentration and found no change in the formation numbers over the range $[Cu]_T$ = 0.02–0.08 M. From a consideration of the precision of the experiments, we have calculated a lower limit $\log K_{DO}^{Cu} \geq 0.2$ at 25 °C (I = 3.0 M) (see eq 2). Actual values of K_{DO}^{Cu} can be estimated

$$Cu_2(OAc)_4(aq) \overset{K_{DO}^{Cu}}{\rightleftharpoons} 2Cu(OAc)_2(aq) \qquad (2)$$

roughly by two independent methods. The solubility of copper(II) acetate hydrate in water is 0.38 M at 25 °C.[7] Estimating concentrations of monomer complexes in the saturated solution, with appropriate stability constants,[8] we obtain $\log K_{SD}^{Cu} = -1.4$ (see eq 3).

$$Cu_2(OAc)_4(OH_2)_2(s) \overset{K_{SD}^{Cu}}{\rightleftharpoons} 2Cu(OAc)_2(aq) \qquad (3)$$

Chromium(II) acetate is much less soluble,[5] and in view of the structural similarity of the two solids,[1,2] it seems reasonable to assume that, in the absence of the dissociation reaction (2), the copper complex would have had the same solubility, i.e., that $\log K_{SO}^{Cu} = -2.7$ (see eq 4). Combining eq 3 and 4 then

$$Cu_2(OAc)_4(OH_2)_2(s) \overset{K_{SO}^{Cu}}{\rightleftharpoons} Cu_2(OAc)_4(aq) \qquad (4)$$

gives $\log K_{DO}^{Cu} = 1.3$.

In acetic acid–water media, equilibrium 5 has been directly

$$Cu_2(OAc)_4 + 4H_2O \overset{K_D'}{\rightleftharpoons} 2Cu(OAc)_2(OH_2)_2 \qquad (5)$$

observed,[10] with $\log K_D' = -5.0$ at 25 °C. The experimental data cover the range $[H_2O]$ = 0–10 M only, but on extrapolating to aqueous solution by substituting $[H_2O]$ = 55.5 M, we obtain $\log K_{DO}^{Cu} = 2.0$. Thus both estimates are consistent with the lower limit given above, though the agreement between them must be fortuitous.

The greater stability of the chromium complex must be due to a stronger metal–metal bond. Metal–oxygen bonding is important in both complexes but is expected to act in the opposite sense, since complexes of copper(II) are characteristically more stable than those of chromium(II). This effect can be roughly quantified by noting that the dimers $M_2(OAc)_4$ contain eight cation–anion "half-bonds", while the monomers $M(OAc)_2$ contain two full bonds. Taking the gross stability constants $\log \beta_2^{Cr} = 1.9$[5] and $\log \beta_2^{Cu} = 2.7$[6] suggests that metal–oxygen bonding destabilizes the chromium(II) dimer relative to the copper(II) dimer by about 2(2.7 − 1.9) = 1.6 units in the logarithm of the equilibrium constant. Hence the true difference between the Cr–Cr and Cu–Cu bonds is of the order of 4.4 + 2.0 + 1.6 = 8.0 units.

For the copper dimer, magnetic[11-13] and spectroscopic[14,15] data are generally interpreted in terms of a very weak Cu–Cu interaction, a δ bond formed by overlap of the metal $d_{x^2-y^2}$ orbitals. For the chromium dimer, the interaction is accepted to be stronger and more complex. It is usually described as a quadruple bond, with one σ, two π, and one δ component,[11,16] though admittedly[17] not so strong as the interaction in the isoelectronic Mo–Mo[3] and Mo–Cr[4] compounds. What the present calculations show is that, in spite of a difference of three units in bond order, the Cr–Cr bond in the acetate system is stronger than the Cu–Cu bond by only about 45 kJ mol^{-1}.

Registry No. $Cr_2(OAc)_4$, 15020-15-2; $Cu_2(OAc)_4$, 23686-23-9.

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Microwave Spectrum, Dipole Moment, and Conformation of Vinyldifluorophosphine

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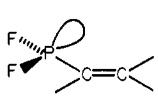
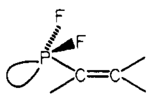
The synthesis of vinyldifluorophosphine ($PF_2C_2H_3$) was reported by Centofanti and Lines.[1] A molecular symmetry of C_s would be expected for it since this is often found in PF_2 derivatives such as PF_2NH_2[2] and PF_2OCH_3.[3] It is more difficult to anticipate whether the predominant conformer is I or II. We report the assignment of the microwave spectrum and find that the rotational constants are consistent with I.



I



II

Experimental Section

Sample. The compound was prepared according to the literature synthesis.[1] It was difficult to handle the starting material $Hg(C_2H_3)_2$ and to avoid its vile odor during transfer and clean up. Consequently, enriched syntheses were not attempted.

Spectrometers. A conventional 80-kHz Stark modulated spectrometer with klystron sources and a Hewlett-Packard 8460A spectrometer system[4] were employed to record the spectra at −78 °C. Transition frequencies are believed to be accurate to ±0.1 MHz.

Spectra. A μ_a-type spectrum was observed with clustering of transitions at intervals of about 5 GHz. The regions between these intervals were generally sparse. A clear set of 2 or 3 vibrational satellite lines were observed on the high-frequency side of each strong ground-state line. The assignment of transitions was based on their Stark effects and the frequency fit. Only μ_a transitions could be found indicating that μ_b and μ_c were very small.

Several of the assigned transitions and the rigid rotor rotational constants derived from them are listed in Table I. A complete list of observed transitions for the ground state and first three vibrational states is given in Tables S1 and S2 (available as supplementary material). The complete set of frequencies was fit with use of a first-order centrifugal distortion analysis program, provided by Thomas.[5] The effective semirigid rotor constants derived from this set (Table S3, available as supplementary material) differed from

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