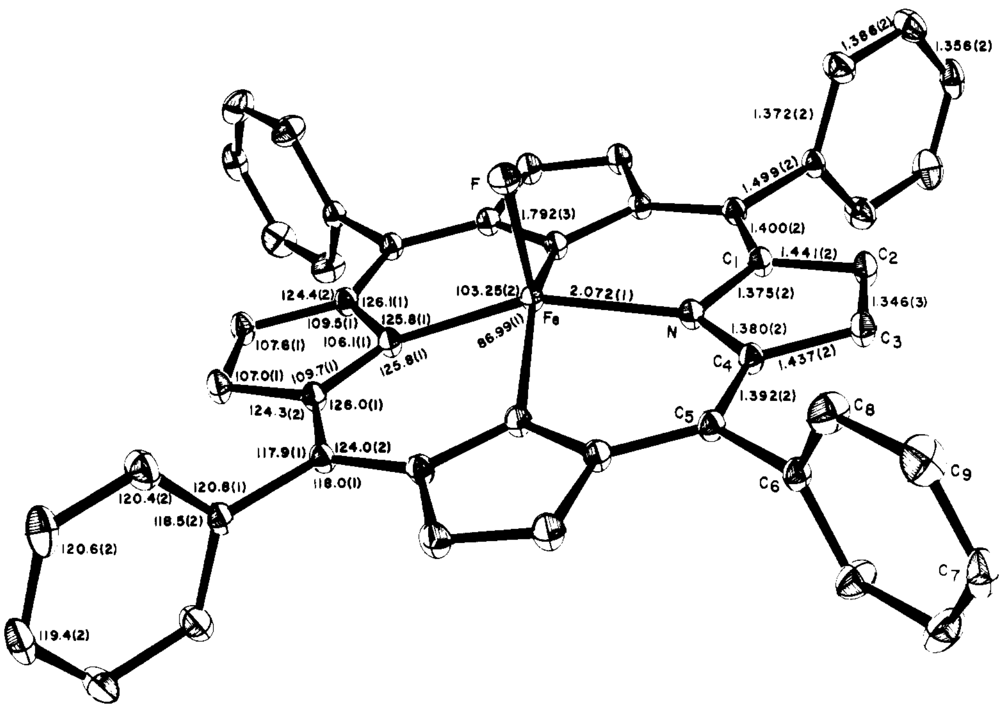

Figure 2. Computer-drawn view of the Fe(TPP)(F) molecule. The numbering scheme for the crystallographically unique atoms is shown as are the individual bond distances and angles with their respective estimated standard deviations.

associated thermal parameters are reported in Table I. A listing of the final observed and calculated structure amplitudes (×10) is available as supplementary material.

Results and Discussion

Figure 2 presents a perspective view of the Fe(TPP)(F) molecule. The figure also illustrates the numbering scheme employed for the unique atoms and the individual values for the bond distances and angles in the molecule. A table of values is also given in the supplementary material. In space group $I4/m$, the Fe(TPP)(F) molecule is disordered with statistical $4/m$—C_{4h} symmetry. The porphinato core in Fe(TPP)(F) thus has crystallographically required planarity. The anisotropic temperature factors (Table I) do not appear to be disguising any significant nonplanarity of the core.

The coordination group parameters for Fe(TPP)(F) are typical of those for a high-spin five-coordinate (porphinato)iron(III) complex.[16] Table II summarizes four coordination group parameters for the (porphinato)iron(III) halide complexes.[17] The parameters are the average Fe–N bond distance, the iron to axial ligand distance, the displacement of the iron(III) atom from the mean plane of the four nitrogen atoms and the mean plane of the core. In Fe(TPP)(F) and Fe(TPP)(Cl), these two displacements are equal because of the planarity of the respective cores. It can be seen that the displacements in Fe(TPP)(Cl) are smaller than any other derivative; it is possible that this smaller displacement is a consequence of molecular packing.[18]

The axial Fe–F distance of 1.792 (3) Å in Fe(TPP)(F) is significantly shorter than the value normally observed, about 1.92 Å, for terminal Fe–F distances in polymeric fluorides[19] or in monomeric octahedral complexes.[20] It was originally noted by Hoard[16] that the axial distances in high-spin five-coordinate (porphinato)iron(III) complexes are particularly short. This pattern persists for all the halide derivatives listed in Table II.

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Registry No. Fe(TPP)F, 55428-47-2; [Fe(TPP)]$_2$O, 12582-61-5.

Supplementary Material Available: Table III, bond distances and angles in Fe(TPP)(F), and a listing of structure factor amplitudes (×10) (6 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry,
Auburn University, Auburn, Alabama 36849, and
University of Birmingham, Birmingham B15 2TT, U.K.

Conformation of Tris(dimethylamino)phosphine: An MNDO Study

S. D. Worley,*[1a] J. H. Hargis,[1a] L. Chang,[1a]
and W. B. Jennings[1b]

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The molecular conformations of aminophosphorus(III) compounds have attracted quite a bit of attention recently. The various conformational models (drawn with planar nitrogens) are shown in Figure 1. Model compounds have been prepared which contain nitrogen "lone-pair" orbitals whose

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(1) (a) Auburn University. (b) University of Birmingham.

Table I. MNDO Heats of Formation[a] and Ionization Energies[b] for Tris(dimethylamino)phosphine (1) in Various Conformations

model	ϕ_{PN}[c]	symmetry	geometry at N[d]	ΔH_f	I_1	I_2	I_3	I_4
A	90, 90, 90	C_{3v}	p[e]	−44.93	9.54	9.73	9.76	10.82
B	90, 90, 0	C_s	p	−43.77	9.31	9.61	9.78	11.24
B	90, 90, 0	C_s	np	−44.06	9.22	9.56	9.85	11.33
C	90, 0, 0	C_s	p	−32.83	9.11	9.56	9.74	11.51
C	90, 0, 0	C_s	np	−33.17	8.93	9.60	9.81	11.82
D	0, 0, 0	C_{3v}	p	−2.93	8.99	9.51	9.51	11.72
D	0, 0, 0	C_{3v}	np	−4.77	8.77	9.60	9.61	12.05
E	61, 61, 61	C_3	p	−46.25	9.34	9.70	9.70	11.12
E	61, 61, 61	C_3	np	−47.10	9.18	9.78	9.78	11.33
exptl[f]					7.59	7.91	8.75	9.89

[a] kcal mol^{-1}. [b] Koopmans' theorem values in eV. [c] Dihedral angles (deg) between the phosphorus and nitrogen lone pairs. [d] p = planar at N; np = optimized geometry at N. [e] Nitrogens optimized at planar geometry. [f] Reference 10.

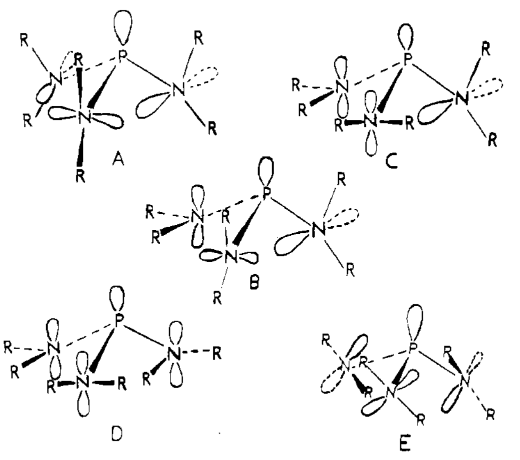

Figure 1. Possible conformational models for tris(dimethylamino)phosphine.

relative orientations are approximately those of models A and C in Figure 1. For example, Cowley and co-workers have reported the ultraviolet photoelectron spectra (UPS) for a series of bicyclic caged aminophosphines for which model A must apply.[2] Extensive work in these laboratories concerning the photoelectron spectra,[3] low-temperature NMR,[4,5] and molecular orbital calculations[6] has been performed for a series of diazaphospholanes whose conformations are represented essentially by model C. However, there remains some controversy concerning the conformation of acyclic tris(dialkylamino)phosphines, especially for the title compound (**1**). Vilkov and co-workers have suggested that **1** contains a C_3 symmetry axis (model E in Figure 1) on the basis of electron diffraction investigations.[7] Several laboratories have studied the photoelectron spectra of **1** and various related molecules.[8-10] Cowley and co-workers[8] assumed model B (Figure 1) in their interpretation of the UPS of **1**, while Lappert and co-workers[9] have suggested that model D could equally well fit the data. UPS work in these laboratories indicated that model B gave the best fit of the data for several tris(dialkylamino)phosphines in accord with the studies of Cowley et al. but that the ordering of the lone-pair orbitals suggested by these workers should be revised.[10] Recent UPS work on the chromium pentacarbonyl complex of **1** has been interpreted to support the original Cowley assignments.[11] An X-ray diffraction analysis has shown that tris(piperidino) and tris(morpholino) analogues of **1** adopt a geometry close to that of model B but with nonplanar nitrogens.[12] The most recent developments in the controversy concerning **1** have been an X-ray structure determination of the iron tricarbonyl complex of **1** and ab initio MO calculations at the STO-3G level for the parent molecule $(H_2N)_3P$ by Cowley and co-workers.[13] These studies, although unfortunately not on **1** itself due to the facts that **1** becomes a glass at low temperature and that an ab initio calculation on **1** would be prohibitive at this time due to its size, proved that the conformational energies of models B and E are very close.

The current work represents an extensive MNDO computational study of the models A–E for **1**. The MNDO SCF–MO method developed by Dewar and co-workers[14] is an extremely useful semiempirical SCF–MO procedure because it contains a geometry-optimization feature and thus is not dependent upon model-compound geometries or upon experimental data that may not be available. Furthermore, it treats large molecules such as **1** rapidly and efficiently. Work in these laboratories has already demonstrated the ability of MNDO to reproduce accurately P–N conformations in several aminophosphorus(III) compounds,[6] inversion barriers in trivalent nitrogen compounds,[15] and orbital-energy ordering in various systems.[16,17]

Results and Discussion

Several types of computations were performed in this study for models A–E. In one series of calculations the nitrogens were held planar while all other geometric parameters were optimized except the dihedral angles between the C–N bonds and the phosphorus lone pair. The latter was fixed in order to maintain a particular conformational model. In another series of calculations the nitrogen geometries were allowed to optimize out of plane, while the dihedral angle between the nitrogen and phosphorus lone pairs was maintained at the value appropriate to each model. The heats of formation and the four highest occupied orbital energies (the "lone-pair" orbitals) calculated for each model are given in Table I. As can be

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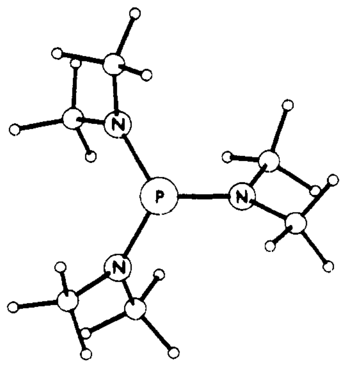

Figure 2. A projection of the optimized MNDO geometry (model E) of $P(NMe_2)_3$, viewed down the C_3 axis.

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 $P[N(Me)CH_2]_3CMe$ 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.

Contribution from the School of Chemical Sciences,
University of East Anglia, Norwich, NR4 7TJ, England

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

Roderick D. Cannon

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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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