geometric optimization, carbene energies were calculated with the split-valence 4-31G basis set.[15] (b) Rotation of the cyclopropyl group of **1b** about the σ bond to the carbenic center by 180° produces a new "bisected" conformer which is calculated to be 2.5 kcal/mol more energetic than **1b**.

(17) The carbenes were 1, $ClCCH_3$; 2, FCPh; 3, $ClCSCH_3$; 4, CCl_2; 5, FCCl; 6, CF_2; 7, $ClCOCH_3$; 8, $FCOCH_3$; 9, FCOH; 10, $C(OCH_3)_2$; 11, $C(OH)_2$; 12, $CH_3OCN(CH_3)_2$.

(18) The analytical form of Figure 2 is $\Delta E_{stab} = 28.6 m_{CXY} + 12.8$.

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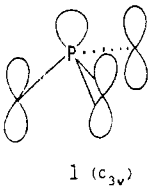
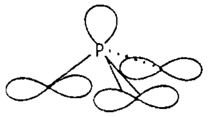
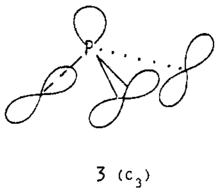
Conformation of Ligated Tris(dimethylamino)phosphine

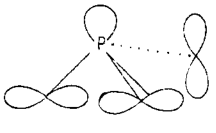
Sir:

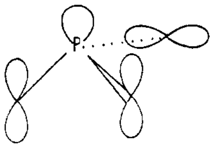
The electronic and molecular structures of tris(dialkylamino)phosphines have attracted attention recently. Several symmetrical conformations, such as **1–5**, can be considered for this class of molecule.[1] In an electron diffraction study, Vilkov and co-workers[2] concluded that the geometry of $(Me_2N)_3P$ is **3**. In 1973 the ultraviolet photoelectron spectrum (UV PES) of $(Me_2N)_3P$ was measured and interpreted according to structure **4**.[3] In subsequent UV PES work Lappert and co-workers[4] concluded that the structure of $(Me_2N)_3P$ could be C_{3v} (**1**) and suggested that the pattern of low ionization peaks may be due to Jahn–Teller splitting of the ^2E state of the radical cation rather than to the adoption of the C_s ground-state geometry, **4**. In 1977 UV PES work on tris(dialkylamino)phosphines, Hargis and Worley[5] concluded that our original model was correct but presented a slightly different spectral assignment. In the most recent UV PES work on free and coordinated $(Me_2N)_3P$, Yarbrough and Hall[6] concluded that our original assignments were correct. To probe this question further we have performed molecular orbital (MO) calculations on the model compound, $(H_2N)_3P$, and determined the X-ray crystal structure of $[(Me_2N)_3P]_2Fe(CO)_3$.[7,8]


1 (C_{3v})


2 (C_{3v})


3 (C_3)


4 (C_s)


5 (C_s)

The MO calculations on $(H_2N)_3P$ were performed with the GAUSSIAN 76[9] and the FORCE[10] programs using STO3G and STO3G* basis sets. Regardless of the presence or absence of d orbitals in the basis set, the C_3 conformation, **3**, emerged as the most stable. However, the geometry-optimized structures corresponding to the C_3 (**3**) and C_s (**4**) conformations are rather close in energy.[11] With the STO3G basis set conformation **3** is computed to be more stable than **4** by 3.53 kcal/mol, while with the STO3G* basis set the energy difference is reduced to 1.19 kcal/mol.

Colorless crystals of $[(Me_2N)_3P]_2Fe(CO)_3$ were grown from acetone solution. The complex crystallizes in the monoclinic system, space group $P2_1/c$, with 4 molecules per unit cell: $a = 11.177$ (1), $b = 15.778$ (1), $c = 13.270$ (2) Å; $\beta = 90.09$ (1)°. X-ray data were collected on a Syntex $P2_1$ automated diffractometer. The structure was solved by conventional heavy-atom methods using 4233 observed reflections. Full-matrix least-squares refinement afforded a conventional R value of 0.041.

The overall geometry of $[(Me_2N)_3P]_2Fe(CO)_3$ is trigonal-bipyramidal with the aminophosphine ligands occupying axial positions. By far the most interesting structural feature is the fact that the two $(Me_2N)_3P$ ligands adopt different conformations;[12] one (P-1) possesses approximately C_s skeletal symmetry, while the other (P-2) has an unsymmetrical structure of roughly C_3 symmetry (Figures 1 and 2). It seems clear, therefore, that conformations **3** and **4** are rather close in energy as indicated in the MO calculations.

Also significant is the fact that the nitrogen atoms with lone pairs approximately trans (dihedral angle,[13] ϕ ~180°) to the

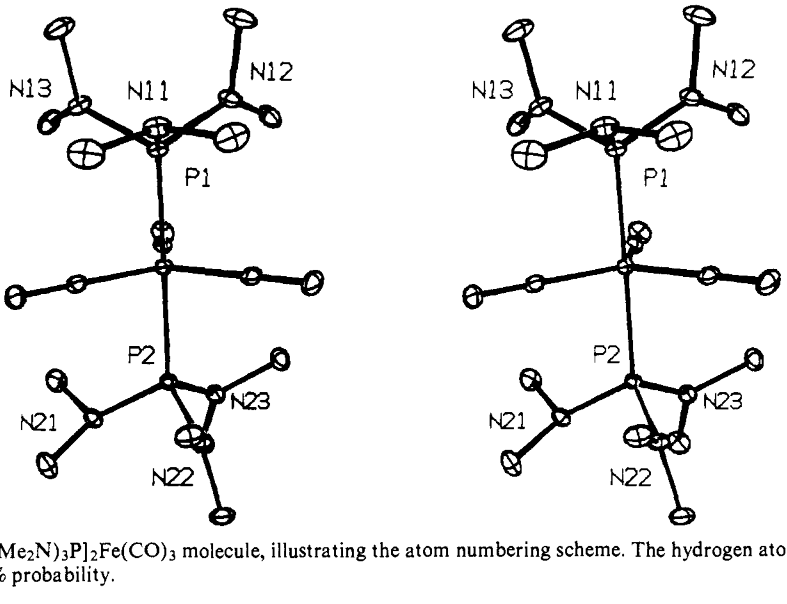


Figure 1. Stereoview of the $[(Me_2N)_3P]_2Fe(CO)_3$ molecule, illustrating the atom numbering scheme. The hydrogen atoms are omitted; all other atoms are shown as ellipsoids of 30% probability.

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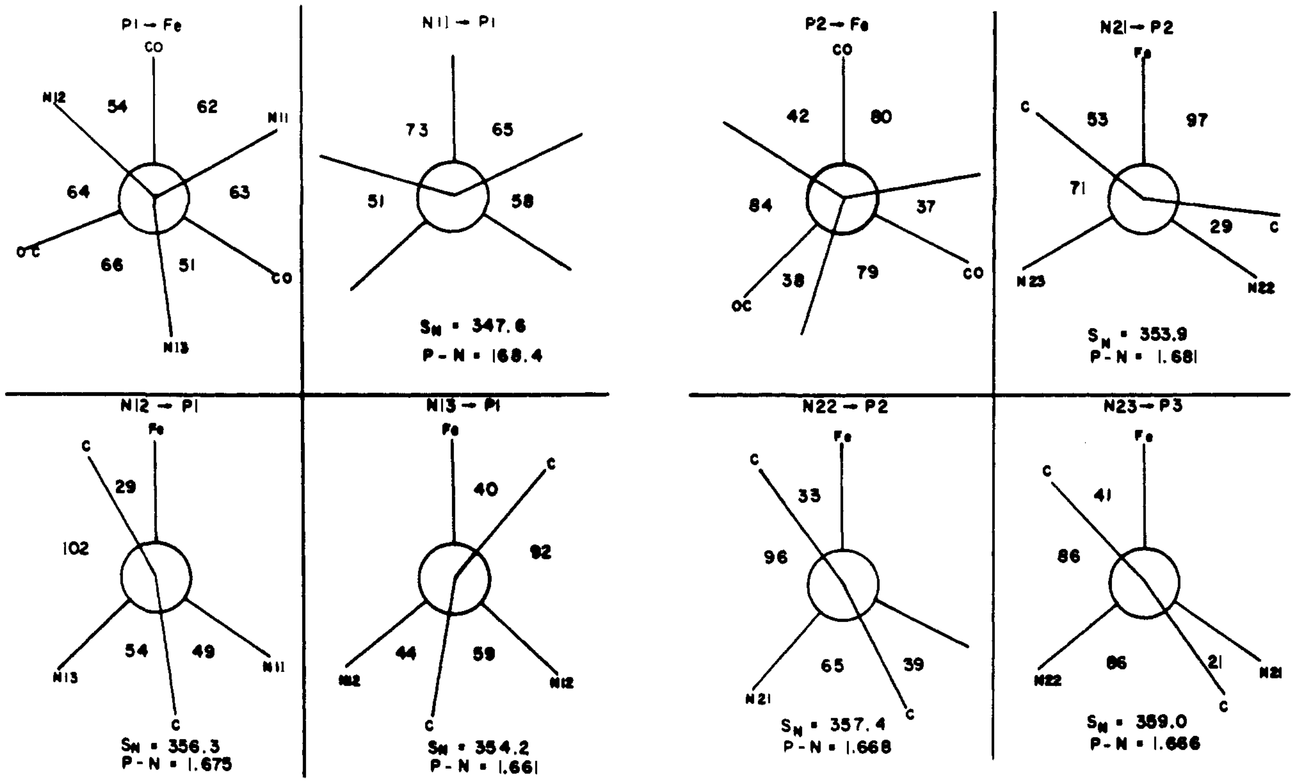

Figure 2. Newman projections down the various P-Fe and N-P bonds of $[(Me_2N)_3P]_2Fe(CO)_3$. The atom numbering scheme is illustrated in Figure 1. S_N represents the sum of bond angles around nitrogen and the N-P bond distances are expressed in angstroms.

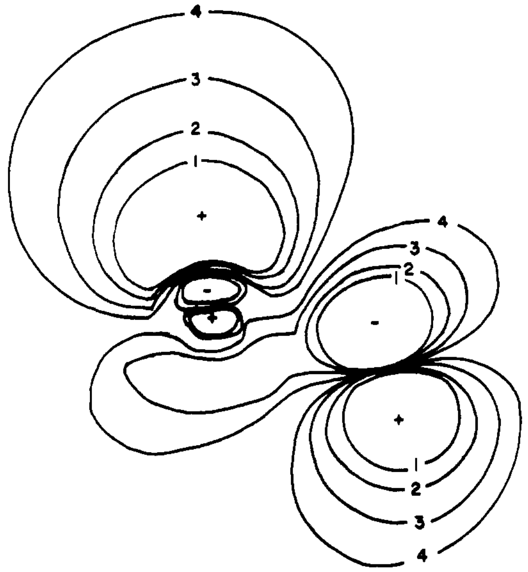

Figure 3. X_α SW contour plot of the HOMO of $(H_2N)_3P$ in the C_s conformation, **4**. Contour values follow: 1 = ±0.10; 2 = ±0.07; 3 = ±0.04; 4 = ±0.02.

P-Fe bond (N-11 and N-21 in Figure 2) exhibit the smallest sum of bond angles (S_N), indicative of a hybridization between sp^2 and sp^3. This observation has a parallel both with the present MO calculations on $(H_2N)_3P$[11] and those published earlier[14] on H_2NPH_2. For both molecules the nitrogen geometry changes from trigonal-planar toward tetrahedral as the dihedral angle[13] increases from 90 to 180°.

The fact that the longest N-P bond distances involve N-11 and N-21 can be understood by appeal to the MO calculations on $(H_2N)_3P$ and H_2NPH_2, which both indicate lengthening of the N-P bond when the dihedral angle changes from 90 to 180°, or by means of qualitative considerations relating N-element bond distances to the percent N(2s) character in the bonding orbitals.

It has been demonstrated[15] that acyclic aminophosphines such as $(Me_2N)_3P$ possess greater Lewis basicities than their bicyclic analogues such as $MeC(CH_2NMe)_3P$. The latter bases possess a local geometry about phosphorus corresponding to **2**.[16] It has been suggested[3b,5,15] that this difference of basicity arises because conformations such as **3** and **4** for the acyclic aminophosphines permit interactions of one or more of the nitrogen lone pairs with the phosphorus lone pair, thereby destabilizing the latter, while in conformation **2** interactions of this kind are precluded by symmetry. This view is confirmed both by the GAUSSIAN 76 and also X_α scattered wave (SW X_α)[17] calculations on $(H_2N)_3P$ which show that the HOMO's of conformations **3** and **4** contain siginificant amounts of phosphorus lone-pair character. An SW X_α contour plot of the HOMO of $(H_2N)_3P$ in conformation **4** is shown in Figure 3.[18]

Acknowledgments. The authors are grateful to the National Science Foundation (Grant CHE76-10331) and the Robert A. Welch Foundation for generous financial support. The Syntex $P2_1$ diffractometer was purchased with funds from NSF Grant No. GP-37028. The authors also express gratitude to Professor M.-H. Whangbo for performing a preliminary conformational study of $(H_2N)_3P$ with the GAUSSIAN 70 program.

References and Notes

(1) The drawings imply that each nitrogen atom is trigonal-planar and that the nitrogen lone pair resides in a pure 2p orbital. This is merely an idealization since, as discussed later, the nitrogen geometry is contingent upon the dihedral angle down the N-P bond.
(2) L. V. Vilkov, L. S. Khaikin, and V. V. Evdokinov, *Zh. Strukt. Khim.*, **10**, 1101 (1969).
(3) (a) A. H. Cowley, M. J. S. Dewar, D. W. Goodman, and J. R. Schweiger, *J. Am. Chem. Soc.*, **95**, 6506 (1973). See also (b) A. H. Cowley, D. W. Goodman, N. A. Kuebler, M. Sanchez, and J. G. Verkade, *Inorg. Chem.*, **16**, 854 (1977).
(4) M. F. Lappert, J. B. Pedley, B. T. Wilkins, O. Stelzer, and E. Unger, *J. Chem. Soc., Dalton Trans.*, 1207 (1975).
(5) J. H. Hargis and S. D. Worley, *Inorg. Chem.*, **16**, 1686 (1977).
(6) L. W. Yarbrough II and M. B. Hall, *Inorg. Chem.*, **17**, 2269 (1978).
(7) Unfortunately, uncomplexed acyclic tris(dialkylamino)phosphines freeze

to glasses at low temperatures, rendering them unsuitable for study by X-ray methods.

(8) The compound $[(Me_2N)_3P]_2Fe(CO)_3$ was prepared by the procedure of R. B. King, *Inorg. Chem.*, **2**, 936 (1963).

(9) J. S. Binkley, R. A. Whiteside, P. C. Hariharan, R. Seeger, J. A. Pople, W. J. Hehre, and M. D. Newton, GAUSSIAN 76 program, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

(10) The program FORCE was written by H. B. Schlegel, Ph.D. Thesis, Queen's University, Kingston, Ont., Canada, 1975. It is based on the method of P. Pulay, *Mol. Phys.*, **17**, 197 (1969).

(11) Conformation **3:** C_3 symmetry; r(NP) = 1.7468, r(NH) = 1.028 Å (av); dihedral angle,[13] ϕ = 88.0°; sum of bond angles around nitrogen, S_N, = 327.4°; total energy, E, = −501.627 006 (STO 3G), −501.731 487 hartrees (STO 3G*). Conformation **4:** C_s symmetry; r(NP) = 1.738 and 1.760, r(NH) = 1.026 (av) and 1.030 Å; ϕ = 91.4, 180°; S_N = 333.9, 322.6°; E = −501.621 449 (STO 3G), −501.729 589 hartrees (STO 3G*).

(12) There are no intermolecular contacts shorter than the sums of the respective van der Waals radii. The observed molecular geometry is therefore not affected appreciably by interactions between molecules. A complete discussion of inter- and intramolecular effects will appear in a full paper.

(13) The dihedral angle, ϕ, is taken to be the angle between the planes bisecting the X-N-X (X = C,H) and N-P-N bond angles viewed down the N-P bond.

(14) A. H. Cowley, M. W. Taylor, M.-H. Whangbo, and S. Wolfe, *J. Chem. Soc., Chem. Commun.*, 838 (1976).

(15) (a) R. D. Kroshefsky and J. G. Verkade, *Inorg. Chem.*, **14**, 3090 (1975); (b) J. G. Verkade, *Phosphorus Sulfur*, **2**, 251 (1976), and references therein.

(16) The molecular geometry of $MeC(CH_2NMe)_3P$ has not been determined by X-ray crystallography; however, the corresponding phosphine oxide and phosphine-borane complexes have been characterized structurally and found to possess a local phosphorus geometry corresponding to **2**. See J. C. Clardy, R. L. Kolpa, and J. G. Verkade, *Phosphorus*, **4**, 133 (1974). Owing to the constraints of the cage system it is safe to assume that the same conformation persists in the parent phosphine.

(17) (a) J. C. Slater and K. H. Johnson, *Phys. Rev., B*, **5**, 844 (1972); (b) J. C. Slater, "Quantum Theory of Molecules and Solids", Vol. **4**, McGraw-Hill, New York, 1974, p 583.

(18) NOTE ADDED IN PROOF. The X-ray crystal structure of $(Me_2N)_3PFe(CO)_4$ has now been determined and is undergoing refinement (present R = 0.083). The aminophosphine geometry in $(Me_2N)_3PFe(CO)_4$ is virtually identical with that of P-2 in $[(Me_2N)_3P]_2Fe(CO)_3$ and may be described as approximately conformation **3** with two Me_2N groups nearly planar and twisted in the same direction ($\phi \simeq$ 90–100°), but with the third such group at $\phi \simeq$ 180° much more pyramidal. This lends further credence to our assertion[12] that the observed conformations and distortions from planarity of the Me_2N groups are not due to interactions between molecules. Structural details of both compounds will be discussed in a forthcoming paper.

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Anion-Radical Crystal Lattice Energies

Sir:

The factors that control the thermodynamic stability of organic anion radicals can be broken down into two major categories: those that are intramolecular and those that are intermolecular in nature. The major intramolecular consideration is the electron affinity of the neutral molecule, while the intermolecular factors for solvated anions include anion solvation and ion association with the cation. However, in the solid phase the only intermolecular factor is the crystal lattice energy (U_0).

The classic work of Brauman and Blair[1] has demonstrated the vital importance of solvation in controlling the thermodynamic stability of solvated anions. However, there has been very little work concerning the crystal lattice energies of solid organic salt systems. Here we report the first crystal lattice energy measurements for anion-radical salts and show that this crystal lattice energy is much more important in controlling the thermodynamic stability of the salt than are the intramolecular effects.

Since it has been well established that the exclusive organic products resulting from the reactions of the anion radicals of anthracene (AN) and tetracene (TE) are 9,10-dihydroanthracene (ANH_2)[2] and 9,10-dihydrotetracene (TEH_2),[3] respectively, the enthalpy of this reaction was measured and used in a thermochemical cycle to obtain the heats of formation and the crystal lattice energies of the solid sodium anion-radical salts.

The anion radicals of AN and TE were generated under high vacuum in tetrahydrofuran (THF) via reduction with a difficient amount of sodium metal. Once the entire sodium mirror had dissolved, the THF was evaporated from the solution under vacuum leaving the solid anion-radical salts. These solid salts were then left open to high vacuum for at least 48 h with two liquid nitrogen traps between the vacuum pump and the salt container to ensure complete removal of the solvent. The desolvated solid anion-radical salts were then placed into thin-walled evacuated glass bulbs, which were subsequently sealed off from the apparatus. The thin-walled bulbs were then placed into a Parr solution calorimeter and broken under 100 mL of deoxygenated water with a push rod. The change in the temperature of the calorimeter was due strictly to the reaction of the anion-radical salt with the water to produce the dihydro hydrocarbon and sodium hydroxide:

$$2Na^+AN^{-\cdot}{}_{(solid)} + 2H_2O_{(liq)} \rightarrow 2NaOH_{(aq)} + AN_{(solid)} + ANH_{2(solid)} \quad (1)$$

$$2Na^+TE^{-\cdot}{}_{(solid)} + 2H_2O_{(liq)} \rightarrow 2NaOH_{(aq)} + TE_{(solid)} + TEH_{2\,(solid)} \quad (2)$$

The only organic compounds remaining in the calorimeter after the reaction are the neutral hydrocarbon and the dihydro hydrocarbon. The possibility of the evolution of hydrogen gas from the reaction with water was eliminated by pumping any gaseous products into a calibrated gas buret with a Toepler pump as previously described.[4] The fact that no gas-phase products could be detected means that at least 99.9% of the reaction leads to protonation of the anion radicals. Deuterated water was added to several samples of the anion-radical solid salts. Subsequent NMR analysis of these D_2O solutions showed no traces of THF, indicating that this solvent is not coordinated into the crystal lattice structure of the salt.

The calorimeter contents were titrated with standardized HCl solutions after each experiment. The number of millimoles of NaOH present in the water was considered to be equal to

Table I. Enthalpies of Reaction in Kilocalories/Mole

reaction	π, $\Delta H°$ AN	π, $\Delta H°$ TE	ref
$\frac{1}{2}\pi H_{2\,(solid)} + \frac{1}{2}\pi_{(solid)} + NaOH_{(aq)} \rightarrow Na^+\pi^{-\cdot}{}_{(solid)} + H_2O_{(liq)}$	+41.1	+33.4	this work
$Na^0{}_{(solid)} + H_2O_{(liq)} \rightarrow NaOH_{(aq)} + \frac{1}{2}H_2(g)$	−44.1	−44.1	8
$\frac{1}{2}\pi_{(solid)} + \frac{1}{2}H_{2\,(g)} \rightarrow \frac{1}{2}\pi H_{2\,(solid)}$	−8.5	−6.25	9, 13
$\pi_{(g)} \rightarrow \pi_{(solid)}$	−23.5	−29.8	14, 12
$Na^0{}_{(g)} \rightarrow Na^0{}_{(solid)}$	−25.9	−25.9	10
$Na^+{}_{(g)} + e^-{}_{(g)} \rightarrow Na^0{}_{(g)}$	−118.4	−118.4	11
$\pi^{-\cdot}{}_{(g)} \rightarrow \pi_{(g)} + e^-{}_{(g)}$	+12.7	+26.45	12
$Na^+{}_{(g)} + \pi^{-\cdot}{}_{(g)} \rightarrow Na^+\pi^{-\cdot}{}_{(solid)}$	−166.6	−164.6	

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