An *Ab Initio* LCAO–MO–SCF Study of Methinophosphide and Its Relation to Hydrogen Cyanide

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Abstract: LCAO–MO–SCF studies have been carried out on the molecule HCP in four different Gaussian basis sets, three with and one without a d orbital on the phosphorus. A relatively well-balanced basis set appears to be the one having nine s, five p, and one d exponents for the phosphorus, five s and two p for the carbon, and three s for the hydrogen. This gives a calculated dipole moment of 0.11 as compared to the experimental value of 0.34. Three-dimensional plots of the electron density are shown for the entire molecule as well as for each of the valence molecular orbitals, and these are compared with similar plots for HCN calculated for a comparable basis set.

Methinophosphide is the phosphorus analog of hydrogen cyanide and was first prepared[2] in 1961. This monomeric molecule is an unusual one in that it is the only known isolated compound in which phosphorus is bonded to only one neighboring atom rather than to the usual complement of three, four, or five, and sometimes two or six. Presumably, there is a carbon-to-phosphorus triple bond involving phosphorus p orbitals and this is also a chemical novelty. Because of its unusual structure, methinophosphide seemed to be an ideal candidate for a quantum mechanical study.

Calculational Details

The LCAO–MO–SCF calculations were done with uncontracted Gaussian-type orbitals on a Control Data 6600 computer using the program MOSES,[3] with numerous changes and improvements being made to this program by present and former members of our group. When d orbitals are employed with the version of MOSES we use, they are couched in terms of d_{x^2}, d_{y^2}, d_{z^2}, d_{xy}, d_{xz}, and d_{yz}. When these are converted to the usual spherical-harmonic representation involving five d orbitals, a 3s orbital exhibiting the same exponents as were used for the d's also results. The exponents of the s and p orbitals were obtained from atom optimization and are shown in Table I. The exponents for the carbon atom were taken from the literature,[4,5] whereas those for the phosphorus were calculated in our laboratory using program ATOM–SCF.[6] The phosphorus d-orbital exponent in all of the basis sets was chosen to be 0.33 by extrapolation of results obtained from molecular optimization in the phosphine[7] and phosphine oxide[8] molecules. Using a (731) basis[9] for the phosphorus, the d-orbital exponent was found to be 0.34 for PH_3 and 0.25 for OPH_3. In a (951) basis, this exponent was 0.35 for PH_3. It should be noted in Table I that, below the energy shown for the phosphorus in a given basis set, a second slightly lower value of the energy is presented in parentheses. This second value corresponds to the addition of a 3s orbital having an exponent of 0.33 to the set of s and p exponents used as the basis set. This energy given in parentheses is the proper one to be used in calculating binding energies when a d orbital with a coefficient of 0.33 is employed, using our system in which the d orbitals are expressed in terms of d_{x^2}, d_{y^2}, d_{z^2}, d_{xy}, d_{xz}, d_{yz}, which is equivalent to the usual spherical harmonic set of five d orbitals plus a 3s orbital.

Table I. Atom-Optimized Exponents and the Corresponding Total Atomic Energies for the Various Basis Sets Employed

Atom	Basis	Energies, au	Gaussian exponents
H	(2)	−0.4807	s 1.800, 0.2700
H	(3)	−0.4970	s 4.239, 0.6577, 0.1483
C	(52)	−37.5131	s 381.0, 59.18, 13.79, 3.833, 0.2946 p 1.556, 0.2795
C	(73)	−37.6551	s 994.7, 160.0, 39.91, 11.82, 3.698, 0.6026, 0.1817 p 4.279, 0.8699, 0.2036
N	(52)	−54.0784	s 553.3, 84.91, 19.62, 5.421, 0.4201 p 2.333, 0.4148
P	(73)	−338.1905 (−338.2257)[a]	s 4449, 670.7, 157.30, 43.21, 13.342, 2.740, 0.2036 p 18.122, 3.606, 0.2662
P	(95)	−340.4537 (−340.4558)[a]	s 7392, 1133.8, 272.1, 80.35, 26.38, 5.440, 2.053, 0.3570, 0.1552 p 77.68, 18.146, 5.448, 1.7764, 0.2321

[a] Value with an added 3s-type Gaussian for which the orbital exponent is 0.33 (see text).

The geometries used in this study were obtained from microwave investigations of the PCH[10] and HCN[11] molecules. In our calculations, the linear PCH or HCN molecule was put on the positive z axis with the phosphorus or nitrogen at the origin. In PCH, the

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[6] B. Roos, C. Salez, A. Veillard, and E. Clementi, "A General Program for Calculation of Atomic SCF Orbitals by the Expansion Method," IBM Research Laboratory, San Jose, Calif. 95114.

[7] J.-B. Robert, H. Marsmann, L. J. Schaad, and J. R. Van Wazer, *J. Phys. Chem.*, submitted for publication.

[8] H. Marsmann, L. C. D. Groenweghe, L. J. Schaad, and J. R. Van Wazer, *J. Amer. Chem. Soc.*, **92**, 6107 (1970).

[9] The notation (*abc*/*ef*/*g*) indicates that in methinophosphide there are *a* Gaussian orbital exponents of the s type, *b* of the p type, and *c* of the d type for the phosphorus atom, *e* of the s type and *f* of the p type for the carbon, and *g* of the s type for the hydrogen. In the case of the phosphorus atom, the notation is (*abc*).

[10] J. K. Tyler, *J. Chem. Phys.*, **40**, 1120 (1964).

[11] J. W. Simmons, W. E. Anderson, and W. Gordy, *Phys. Rev.*, **86**, 1055 (1952).

Table II. Calculated Data on Methinophosphide in Various Basis Sets

Function	Value			
Gaussian basis	(73/52/2)	(731/52/2)	(951/52/3)	(951/73/3)
Total energy, au	−376.40	−376.48	−378.68	−378.83
Binding energy, eV[a]	5.8	7.2	6.9	7.1
Dipole moment, D (experimental = 0.39)	1.28	1.08	0.11	1.26
P–C overlap, e	1.20	1.55	1.82	1.81
C–H overlap, e	0.78	0.75	0.77	0.64
P–H overlap, e	−0.03	−0.03	−0.03	−0.08
Atomic "charges" [b]				
P atom, e	+0.6	+0.2	+0.1	−0.2
C atom, e	−0.9	−0.4	−0.3	−0.1
H atom, e	+0.3	+0.2	+0.2	+0.3

[a] 1 au = 27.2106 eV. This binding energy represents the differences between the sum of the total energies for the constituent atoms and the total energy for the molecule, all being calculated in the same respective basis sets with no correction for molecular extracorrelation energy.
[b] The formal charge on an atom in a molecule results from subtracting the Mulliken gross atomic population [R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841, 2338, 2343 (1955)] from the atomic number of the chosen atom.

Table III. Orbital Energies (eV) of Methinophosphide in Various Basis Sets

Orbital	Major contribution	(73/52/2)	(731/52/2)	(951/52/3)	(951/73/3)
1σ	P 1s	−2179.2	−2180.7	−2175.6	−2174.9
2σ	C 1s	−309.4	−307.3	−308.8	−308.8
3σ	P 2s	−202.1	−202.8	−204.3	−203.8
4σ	P 2p	−136.6	−137.4	−146.6	−146.1
1π	P 2p	−136.4	−137.1	−146.5	−146.0
5σ	P–C	−26.0	−24.9	−25.8	−26.5
6σ	C–H	−19.1	−18.3	−19.2	−20.0
7σ	P (*lp*)	−11.6	−11.8	−12.5	−12.6
2π	P–C	−9.2	−8.6	−9.5	−10.0

C–P distance was set equal to 1.5421 Å and the H–C to 1.0667 Å. In HCN, the C–N distance was chosen to be 1.156 Å and the H–C to be 1.064 Å.

Results and Discussion

The methinophosphide molecule was first studied in three different basis sets: (73/52/2), (731/52/2), and (951/73/3). Since it appeared on the basis of dipole moment that these basis sets were quite unbalanced, a fourth calculation was carried out using a (951/52/3) basis set. A summary of some of the SCF results for the PCH molecule is presented in Table II for the four basis sets. It is obvious from these results that the best dipole moment is obtained with the (951/52/3) basis set, for which the formal charges on the phosphorus, carbon, and hydrogen atoms also seem quite reasonable.[12] Thus, it appears that this is the best balanced[12,13] of the basis sets used in this study. Note that the binding energies given in Table II are calculated without any correction for the molecular extra-correlation energy.

The orbital energies for methinophosphide in the various basis sets studied are shown in Table III, from which it can be seen that the difference between the energies of a given molecular orbital calculated using different basis sets is reasonably small, except for the 4σ and 1π molecular orbitals, which correspond closely to the inner-shell phosphorus 2p atomic orbitals. This indicates that the chosen basis sets offer a reasonably good representation of the methinophosphide molecule, with the exception that more than three p-type Gaussian exponents are needed to account adequately for the phosphorus "2p" electrons in the (73/52/2) and the (731/52/2) basis sets.

Detailed Mulliken population analyses[14] are shown in Tables IV and V for the methinophosphide molecule. The effect of allowing phosphorus d character is treated in Table V where, in addition, data are given for the two presumably unbalanced basis sets which were investigated with d orbitals. The inner-shell orbitals are omitted from Table V, as the population analysis values for the inner-shell orbitals are equal to the respective values shown in Table IV. By comparing the data given in Tables IV and V for the valence molecular orbitals (5σ through 2π), it is seen that all three basis sets involving a d atomic orbital give quite similar results with respect to the population analysis, except for the 5σ orbital in the (951/73/3) basis set for which the phosphorus gross population is unusually large and the carbon gross population is unusually small. The next largest difference is found for the 7σ overlap populations in this same basis set for which the P–C and the C–H values are out of line.

It is obvious from Table V that the greatest change in gross population upon allowing d character is found for the 5σ molecular orbital for which a couple of tenths of an electronic charge is shifted from the carbon to the phosphorus upon introducing the d function. The greatest change in the shared charges due to the d contribution is found in the 7σ orbital, for which addition of d character converts a rather large negative value for the P–C overlap population to a rather small positive value. In other words, when d character is allowed, the P–C overlap of the 7σ molecular orbital changes from

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(12) M. L. Unland, J. H. Letcher, I. Absar, and J. R. Van Wazer, *J. Chem. Soc. A*, 1328 (1971).
(13) R. S. Mulliken, *J. Chem. Phys.*, **36**, 3428 (1962).
(14) R. S. Mulliken, *ibid.*, **23**, 1833, 1841, 2338, 2343 (1955).

Table IV. Detailed Mulliken Population Analysis for Methinophosphide in a (951/52/3) Basis and for Hydrogen Cyanide in a (52/52/3) Basis

Orbital	Major contribution	Gross population			Overlap population		
		P (or N)	C	H	P–C (or N–C)	C–H	P–H
1σ	P 1s	2.000	0.000	0.000	0.000	0.000	0.000
(1σ)[a]	*N 1s*	*2.008*	*−0.008*	*0.000*	*−0.017*	*0.000*	*0.000*
2σ	C 1s	−0.008	2.008	0.000	−0.019	0.000	0.000
(2σ)	*C 1s*	*0.000*	*2.002*	*−0.002*	*0.000*	*−0.003*	*0.000*
3σ	P 2s	1.999	0.001	0.000	0.002	0.000	0.000
4σ	P 2p	2.001	−0.001	0.000	−0.003	0.000	0.000
1π[b]	P 2p	2.000	0.000	0.000	0.000	0.000	0.000
5σ	P–C	0.831	1.043	0.126	0.631	0.137	0.029
(3σ)	*N–C*	*1.387*	*0.615*	*−0.002*	*0.665*	*−0.002*	*−0.002*
6σ	C–H	0.476	0.986	0.538	0.109	0.575	−0.039
(4σ)	*C–H*	*0.155*	*1.193*	*0.652*	*−0.014*	*0.703*	*−0.020*
7σ	P (*lp*)	1.560	0.330	0.110	0.081	0.054	−0.018
(5σ)	*N (lp)*	*1.740*	*0.168*	*0.092*	*−0.008*	*0.023*	*−0.020*
2π[b]	P–C	1.029	0.971	0.000	0.510	0.000	0.000
(1π)	*N–C*	*0.984*	*1.016*	*0.000*	*0.499*	*0.000*	*0.000*
Total[c]	PCH	+0.081	−0.307	+0.226	1.819	0.765	−0.030
charge	*HCN*	*−0.258*	*−0.002*	*+0.260*	*1.624*	*0.720*	*−0.043*

[a] Values in italics and orbitals shown in parentheses refer to the compound HCN. All other items refer to PCH. [b] The electronic populations are shown for one of the pair of equivalent π orbitals. [c] The values listed under "gross population" are the atomic charges obtained by subtracting the sum of the gross orbital charges for an element from its atomic number.

Table V. Valence-Orbital Atomic Populations of Methinophosphide and Charge Changes upon Allowing Phosphorus d Character

Orbital	Major contribution	Gross population			Overlap population		
		P	C	H	P–C	C–H	P–H
			(731/52/2) Basis				
5σ	P–C	0.90	0.99	0.12	0.62	0.14	0.02
Δ[a]		*0.22*	*−0.19*	*−0.03*	*0.04*	*−0.02*	*0.00*
6σ	C–H	0.51	0.97	0.52	0.12	0.56	−0.03
Δ		*0.08*	*−0.09*	*0.00*	*−0.03*	*−0.02*	*0.00*
7σ	P (*lp*)	1.48	0.40	0.12	0.04	0.06	−0.02
Δ		*−0.01*	*−0.04*	*0.05*	*0.37*	*0.01*	*0.02*
2π	P–C	0.96	1.04	0.00	0.49	0.00	0.00
Δ		*0.08*	*−0.08*	*0.00*	*0.07*	*0.00*	*0.00*
			(951/73/3) Basis				
5σ	P–C	1.18	0.76	0.06	0.50	0.08	+0.00
6σ	C–H	0.45	1.01	0.54	0.10	0.57	−0.04
7σ	P (*lp*)	1.68	0.22	0.10	0.16	−0.01	−0.04
2π	P–C	0.93	1.07	0.00	0.53	0.00	0.00

[a] The values in italics labeled Δ represent the change in electronic charge by allowing d character to the phosphorus atom. They are obtained by subtracting the (73/52/2) values from the respective (731/52/2) values.

rather strong antibonding to a small amount of bonding. It should be noted that the change in overlap population of the P–C π orbital (2π) upon introducing d character is quite small, although the gross populations show some transfer of charge from the carbon to the phosphorus upon allowing d character to the phosphorus. This seems to indicate a change in the overall polarity of the bond without much change in the number of electrons involved in this π bond. In any event, the population analyses show that the 2π molecular orbital clearly corresponds to p_π–p_π bonding between the phosphorus and the carbon, so that the PCH molecule should be characterized as being electronically similar to HCN and may be written as P≡C—H.

Although these SCF molecular orbitals are delocalized, each of the five valence orbitals (5σ through 2π) of methinophosphide is rather well dominated by a particular bonding function. Thus, the population analyses show that the major contribution to the 5σ orbital is P–C σ bonding, while C–H bonding dominates the 6σ orbital. The 7σ orbital has some P–C and C–H σ bonding, but the high gross population on the phosphorus as compared to the carbon and hydrogen shows that the phosphorus lone pair makes a major contribution here. The pair of 2π orbitals corresponds to a P–C triple bond (an equally filled pair of π orbitals).

Since methinophosphide seems to be electronically similar to hydrogen cyanide, an LCAO–MO–SCF calculation was carried out on the latter molecule in a (52/52/3) basis set which should be directly comparable to the (951/52/3) basis for methinophosphide. The total energy found in our calculation on hydrogen cyanide is −92.38 au, which is 0.46 au above the value obtained in another calculation[15] which is probably very close to the Hartree-Fock limit. Pan and Allen[16] have tabulated the data obtained from several different LCAO–MO–SCF calculations on hydrogen cyanide, along with the respective experimental results. The values in their Table III may be compared with the following ones from our (52/52/3) calculation, behind which the experimental data are given in parentheses: dipole moment, 2.50 D (2.99); first ionization potential,

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(15) M. Yoshimine and A. D. McLean, "Computed Ground State Energies and Dipole Moments for Some Linear Molecules," IBM San Jose Laboratory Research Note, Jan 1966.

(16) D. C. Pan and L. C. Allen, *J. Chem. Phys.*, 46, 1797 (1967).

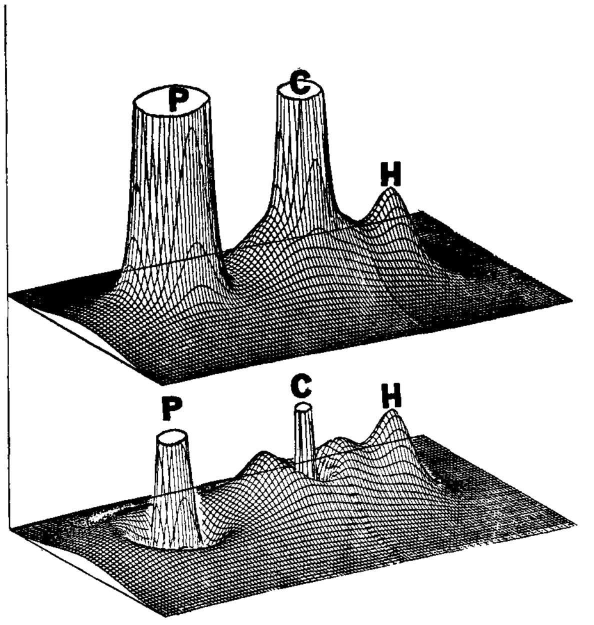

Figure 1. Electron-density (ψ^2) plots for methinophosphide showing the total density (top) and the valence-shell density (bottom). The basal plane of these plots gives the molecular geometry, whereas the vertical axis shows the value of the electron density in the basal plane.

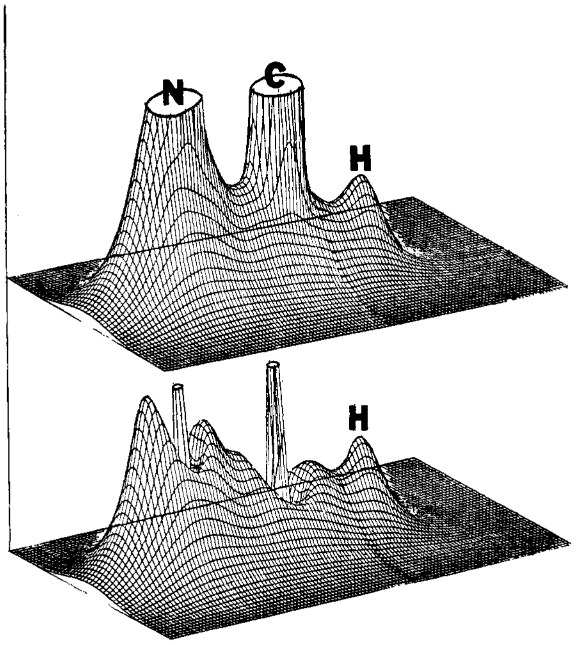

Figure 2. Electron-density plots for hydrogen cyanide showing the total density (top) and the valence-shell density (bottom).

12.9 eV (13.9); and binding energy, 6.31 eV (13.5). In our Table IV, the population analysis for HCN in a (52/52/3) basis is compared oribtal by orbital with that of PCH. It should be noted that, because nitrogen comes from the first row and phosphorus from the second row of the periodic table, the numbering of the related molecular orbitals of PCH and HCN are not the same.

If the P–C and C–H overlap in PCH is compared with the N–C and C–H overlap in HCN, surprisingly little difference is seen (Table IV). The biggest difference in the bonding of these two molecules seems to be in the 6σ molecular orbital of the PCH molecule, which has some P–C in addition to C–H bond character, while the related 4σ orbital in HCN represents a pure C–H bond. The bond polarities are reflected by the gross populations which show, for example, that there is more charge on the carbon than on the phosphorus in the 5σ orbital of PCH, whereas the opposite is true for the related 3σ orbital of HCN. A similar situation is found for the 6σ and 2π orbitals of PCH and the related 4σ and 1π orbitals of HCN. Likewise, the population analysis, in Table IV, of the 7σ orbital of PCH as compared to the 5σ orbital of HCN indicates a greater concentration of electrons in the nitrogen lone-pair position than in that of the phosphorus.

An elegant way of comparing methinophosphide to hydrogen cyanide is by means of three-dimensional electron-density plots in which the basal plane represents the molecular geometry, while the axis perpendicular to it corresponds to the electron density. Figure 1 shows electron-density plots for the total PCH molecule and for its valence orbitals. The annular dips encircling the phosphorus and carbon atoms in the valence-orbital plot are a reflection of the nodes of the respective outer-shell atomic orbitals. Note that the electron density in the bonding region between the phosphorus and carbon is tilted in such a way as to indicate a bond polarity corresponding to the common understanding that carbon is more electronegative than is phosphorus. Likewise, the slope of the electron density along the bond axis at the mid region between the carbon and hydrogen nuclei is in accord with a bond polarity corresponding to carbon having higher electron-withdrawing power than hydrogen.

A similar set of plots to the same scale is shown for hydrogen cyanide in Figure 2. Note the expected reverse in the polarity of the N–C as compared to the P–C bond in the valence-orbital plots. An even more striking difference between Figures 1 and 2 has to do with the lone-pair electrons which are much more diffuse for the phosphorus than for the nitrogen. These lone-pair electrons appear to be more closely held to the nitrogen in HCN than are the lone-pair electrons to the phosphorus in PCH. Although the population analysis shown in Table IV indicates a total of about 0.2 more electron to be involved in P–C overlap than in N–C overlap, comparison of Figures 1 and 2 indicates a considerably less diffuse N–C than P–C bond.

Electron-density plots of the valence molecular orbitals of methinophosphide are shown in Figure 3, while the analogous orbitals for hydrogen cyanide are shown in Figure 4. Inspection of these figures demonstrates clearly that the assignments given in Tables IV and V of the "major contributions" to these orbitals on the basis of the population analysis are borne out by the spacial distributions of the electron densities. Furthermore, Figures 3 and 4 clearly demonstrate the great similarity in electronic structure between methinophosphide and hydrogen cyanide.

Comparison of the 5σ molecular orbital of PCH with the 3σ of HCN shows the opposing polarities of the P–C and N–C σ bonds. Again, it should be noted that there is a much greater density of electrons on the line connecting the nitrogen and carbon nuclei in the 3σ orbital of HCN than in the line connecting the phosphorus and carbon nuclei in the 5σ orbital of PCH even though the N–C overlap was calculated to be 0.665 and

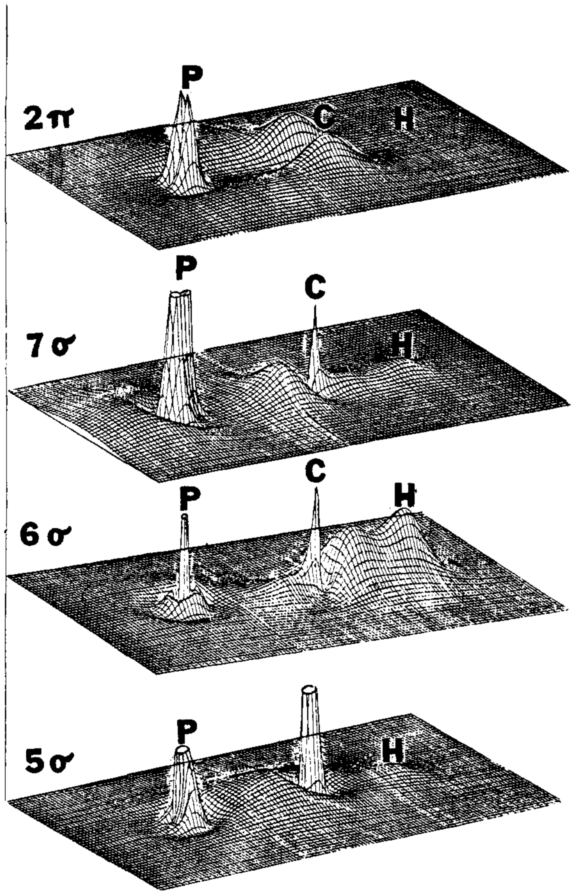

Figure 3. Electron-density plots of the individual valence orbitals of methinophosphide. These orbitals are presented in order of increasing stability, with the one exhibiting the most negative orbital energy at the bottom.

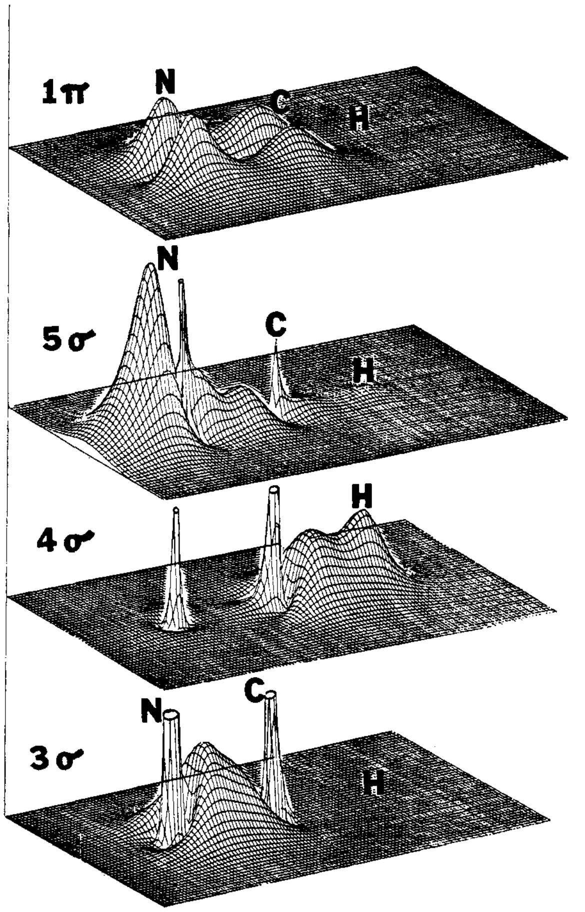

Figure 4. Electron-density plots of the individual valence orbitals for hydrogen cyanide. These orbitals are presented in order of increasing stability, with the one exhibiting the most negative orbital energy at the bottom.

the P–C overlap to be 0.631 for these respective orbitals. The C–H overlap population appearing in the 5σ orbital of PCH may be rationalized as resulting from much greater diffuseness of the P–C σ bond as compared to the N–C σ bond, which is not associated with C–H overlap. We can argue that the diffuseness of the P–C bond is so great that it gives an appreciable electronic charge in the neighborhood of the hydrogen nucleus, which will of course concentrate this negative charge around itself and in the region between it and the carbon to give an appreciable C–H overlap and H gross population.

The 6σ orbital of PCH is, as expected from the population analysis, very similar to the 4σ orbital of HCN. However, the 7σ orbital of PCH, when contrasted with the 5σ orbital of HCN, shows that the nitrogen holds the unshared pair of electrons much more closely than does the phosphorus. The P–C and N–C π-bonding orbitals (2π and 1π, respectively) present an interesting contrast. Although the population analysis of Table V shows that the P–C and N–C overlap populations are nearly identical (with the P–C being somewhat larger), the electron-density plots indicate considerably more compact π bonding between the nitrogen and the carbon as compared to the phosphorus and the carbon.

The appearance of these orbital-density plots is in accord with the magnitudes of their orbital energies in methinophosphide and hydrogen cyanide. For each of the compared valence orbitals, the methinophosphide molecule in a (951/52/3) basis consistently exhibits higher orbital energies than does hydrogen cyanide in a (52/52/3) basis. Thus, the difference in energy between the N–C and P–C π orbitals is 3.4 eV. For the molecular orbitals dominated by the lone pair, the difference is less, corresponding to 1.8 eV; and for the predominately C–H σ-bond orbitals, the difference is 2.2 eV. The greatest difference, 8.4 eV, is found between the orbitals dominated by the C–N and C–P σ bonds. Another feature of Figures 1–4 that should be noted is a consistent error due to the use of a limited number of Gaussian functions. This causes the density surface at the region of the hydrogen nucleus to exhibit a rounded maximum rather than having a pointed top (cusp) as expected on theoretical grounds.

Comparison of the shape of the molecular orbitals of Figures 3 or 4 with the shapes of the orbitals of the free atoms[17] demonstrates that the lobes of the atoms show up in the molecules. We see that the inner lobes, by not being involved in the bonding, act as a "valence-level core" in each valence-shell orbital. This behavior is related to the Mulliken net population but differs primarily in the fact that the lone-pair electrons are separately characterizable in the delocalized molecular orbital electron-density plots.

It is clear from this entire discussion that a Mulliken population analysis has (not unexpectedly) a consid-

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(17) W. T. Bordass and J. W. Linnett, *J. Chem. Educ.*, 47, 672 (1970).

erably lower information content concerning bonding than does an electron-density plot. We believe that a measurement of the axial slope and intensity of the electron density in the center of the bond axis, as well as some measure of the diffuseness of the electrons at right angles to the bond axis at its center, coupled with an indication of how many electrons are involved in the pillar of unshared valence-orbital charge held close to the nucleus, will give a set of four parameters whereby chemical bonds can be readily intercompared (within a given group of basis sets). Further examples of related molecules based on different atoms should be compared in the way PCH and HCN have been contrasted herein in order to see exactly what should be done here.

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Charge-Transfer Integral in Paramagnetic π Molecular Crystals[1a]

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Abstract: An unambiguous separation of charge-transfer (CT) and electrostatic contributions is obtained in aromatic donor–acceptor crystals whose ground states contain stacks of ion radicals, since the activation energy for paramagnetism, ΔE_p, arises from preferential CT stabilization of low-spin states. The magnitude of the Mulliken CT integral, T, is shown to be the geometric mean of ΔE_p and the lowest CT excitation. The values of $|T|$ in aromatic ionic crystals are in good agreement with theoretical estimates of T and of CT stabilization in neutral π molecular dimers.

Electrostatic and charge-transfer interactions both contribute[2] to the stability and geometry of complexes between electron donors, D, and acceptors, A, but their relative magnitudes are difficult to assess.[3] Theoretical treatments are necessarily approximate even for dimers, while experimental studies measure the sum of various contributions.

A clean separation of charge-transfer (CT) contributions is nevertheless possible in π molecular crystals whose ground states contain stacks of ion radicals[4] of the type $\cdots D^+A^-D^+A^-\cdots$. CT interactions between adjacent radicals in a stack preferentially stabilize low-spin configurations and especially the diamagnetic ground state.[5] In the more commonly found *neutral* complexes of diamagnetic D and A molecules, the triplet state D^+A^- involves an electron transfer. Magnetic excitations in ion-radical crystals,[4] on the other hand, require only low-energy spin flips and lead to a temperature dependence of the paramagnetism. Except for a small direct Heisenberg exchange,[4] the observed activation energy ΔE_p for χT, the paramagnetism times the absolute temperature, is solely due to CT contributions[5,6] and measures the thermal equilibrium density of unpaired spins above the diamagnetic ground state.

Electrostatic contributions, by contrast, reflect overall charge densities and are largely independent of spin orientations for small differential overlaps. All intermolecular separations exceed the van der Waals diameter in the π molecular crystals discussed below except at most for the face-to-face separations between molecules in the same stack.[4,5] The differential overlaps are then negligible for molecules in different stacks and small even for adjacent molecules in the same stack.

The temperature dependence of the paramagnetism in ionic π molecular crystals focuses attention on CT interactions and enables us to evaluate the magnitude of the Mulliken CT integral

$$T = \langle D^+A^- | \mathcal{H} | AD \rangle \qquad (1)$$

For largely *neutral* $a\pi$–$b\pi$ dimers in solution, the $|DA\rangle$ ground state contains small admixtures of the singlet excited state $|D^+A^-\rangle$. The *same* CT integral occurs in π molecular crystals with *ionic* ground states and small admixtures of excited neutral contributions.[5,6] We have neglected the effects of the crystalline environment on the molecular orbitals, the usual molecular exciton approximation for small differential overlap. Similar values of T are thus expected in neutral dimers and in ionic crystals when the geometries coincide.

In the following section, we show that the magnitude of T is given by

$$|T| = [\Delta E_p \Delta E_{CT}(\ln 2/0.55x)]^{1/2} \qquad (2)$$

ΔE_p and ΔE_{CT} are the (measured) activation energies for paramagnetism and the lowest CT excitation, respectively. The dissimilarity parameter x is defined by

$$x = 1 + \Delta E_{CT}/\Delta E_{CT}' \qquad (3)$$

and measures the dissimilarity of the radicals in the stack. In $\cdots D^+A^-D^+A^-\cdots$ stacks, ΔE_{CT} corresponds to the CT excitation $D^+A^- \rightarrow DA$, while $\Delta E_{CT}'$

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