of [$HCrO_4^-$], (3.8–4.8) × 10^{-5} *M*, with $Ta_6Cl_{12}^{2+}$ the limiting reagent at *ca.* 1 × 10^{-5} *M*. The kinetic data are consistent with the rate law

$$-d[Ta_6Cl_{12}^{2+}]/dt = k_3[Ta_6Cl_{12}^{2+}][HCrO_4^-][H^+] \qquad (5)$$

with $k_3 = (28 \pm 1) \times 10^3\ M^{-3}\ sec^{-1}$. The range of $HCrO_4^-$ concentrations was too narrow, however, to claim a strictly first-order dependence on [$HCrO_4^-$], although that result would follow by analogy to eq 3.

Reaction Mechanism.—The rate law given in eq 3 indicates the reaction occurs by two parallel pathways, which can be represented by the net activation processes[10]

$$Ta_6Br_{12}^{2+} + HCrO_4^- + H^+ = [(Ta_6Br_{12})H_2CrO_4^{2+}]^{\ddagger} \qquad (6)$$

$$Ta_6Br_{12}^{2+} + 2HCrO_4^- + H^- = [(Ta_6Br_{12})H_3Cr_2O_8^{+}]^{\ddagger} \qquad (7)$$

By analogy to other chromium(VI) oxidations,[7,9,11] a mechanism consisting of a sequence of three one-electron steps can be proposed for the first pathway. In this case, the first step would be

$$Ta_6Br_{12}^{2+} + HCrO_4^- + H^+ \xrightarrow{k_1} Ta_6Br_{12}^{3+} + H_2CrO_4^- \qquad (8)$$

with the two subsequent steps, reduction to Cr(IV) and to Cr(III), being rapid.

Other possibilities must be considered among which is a mechanism involving a rate-determining two-electron step

$$Ta_6Br_{12}^{2+} + HCrO_4^- + H^+ \xrightarrow{k_1} Ta_6Br_{12}^{4+} + Cr(IV) \qquad (9)$$

$$Ta_6Br_{12}^{2+} + Cr(IV) \longrightarrow Ta_6Br_{12}^{3+} + Cr(III) \quad (fast) \qquad (10)$$

$$Ta_6Br_{12}^{2+} + Ta_6Br_{12}^{4+} \longrightarrow 2Ta_6Br_{12}^{3+} \quad (fast) \qquad (11)$$

Provided the first step is the slowest, this is not kinetically distinguishable from the one-electron mechanism. Winograd and Kuwana[12] have studied the rate of reaction 11, finding $k = 9 \times 10^7\ M^{-1}\ sec^{-1}$, which is sufficiently rapid to satisfy that condition. The distinctions that could be made using specific chemical scavenging for Cr(V) and Cr(IV) were not sufficient because of other reactions occurring in this system, as discussed above.

The pathway with a second-order dependence on [$HCrO_4^-$] is probably accounted for by the reaction of dichromate ion, by either of reactions 12 or 13, where

$$\begin{array}{lll} & \nearrow & Ta_6Br_{12}^{3+} + HCr_2O_7^{2-}\ (k_4) \qquad (12) \\ Ta_6Br_{12}^{2+} + Cr_2O_7^{2-} + H^+ & & \\ & \searrow & Ta_6Br_{12}^{4+} + 2Cr(V)\ (k_4) \qquad (13) \end{array}$$

$HCr_2O_7^{2-}$ represents a mixed Cr(VI)–Cr(V) species. On that basis $k_4 = k_2K_d^{-1} = 3.8 \times 10^5\ M^{-2}\ sec^{-1}$. Comparing eq 8 (or 9) and 12 (or 13), which have the same form, it is seen $Cr_2O_7^{2-}$ is considerably more reactive than $HCrO_4^-$, which is not usually the case.[9,13]

The oxidation of $Ta_6Cl_{12}^{2+}$ occurs more rapidly than that of $Ta_6Br_{12}^{2+}$ by a factor of *ca.* 3. This rate difference is in accord with the chloride cluster ion being the stronger reducing agent by *ca.* 0.1 V.[3]

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[10] T. W. Newton and S. W. Rabideau, *J. Phys. Chem.*, **63**, 365 (1959).

[11] J. H. Espenson, *Accounts Chem. Res.*, **3**, 347 (1970).

[12] N. Winograd and T. Kuwana, *J. Amer. Chem. Soc.*, **92**, 224 (1970).

[13] (a) J. H. Espenson and E. L. King, *ibid.*, **85**, 3328 (1963); (b) M. Nicol and D. R. Rosseinsky, *J. Chem. Soc. A*, 2812 (1969).

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Chemical Shifts in Core Electron Binding Energies for Some Gaseous Nitrogen Compounds

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Chemical shifts in core electron binding energies for gaseous nitrogen compounds are compared with values estimated by various theoretical and empirical methods. The relative merits of these methods are discussed.

X-Ray photoelectron spectroscopy is of great interest to chemists because the measured core electron binding energies are a function of the chemical environment of the atoms—that is, the binding energies show chemical shifts. Experimental binding energies for compounds of a given element can be estimated from (1) correlations with calculated atomic charges,[1–6] (2) thermodynamic data based on the approximation that the energy of core electron capture by a nucleus is independent of chemical environment,[7–9] (3) empirical parameters characteristic of the directly bonded groups,[8] and (4)

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[1] K. Siegbahn, *et al.*, "ESCA, Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almqvist and Wiksells, Uppsala, 1967.

[2] J. M. Hollander, D. N. Hendrickson, and W. L. Jolly, *J. Chem. Phys.*, **49**, 3315 (1968).

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[4] M. Pelavin, D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *J. Phys. Chem.*, **74**, 1116 (1970).

[5] D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, **9**, 612 (1970).

[6] K. Siegbahn, *et al.*, "ESCA Applied to Free Molecules," North-Holland Publishing Co., Amsterdam, 1969.

[7] W. L. Jolly and D. N. Hendrickson, *J. Amer. Chem. Soc.*, **92**, 1863 (1970).

[8] W. L. Jolly, *ibid.*, **92**, 3260 (1970).

[9] J. M. Hollander and W. L. Jolly, *Accounts Chem. Res.*, **3**, 193 (1970).

molecular orbital calculated binding energies.[6,10–12]

In order to appraise the relative usefulness of the various methods of estimating chemical shifts, it is important to have chemical shifts that span a wide energy range. We chose to study compounds of nitrogen because of the wide variety of bonding types that they possess and the probability that they would yield a wide range of chemical shifts. We found that the estimation methods that were most readily tested with our data were the atomic charge correlation method and the thermodynamic method. The empirical group parameter method could only be partially tested with our data because, in the set of compounds we studied, many of the groups bonded to nitrogen atoms are unique to those nitrogen compounds. Molecular orbital calculated binding energies are available for only a few of the compounds we studied; however, we hope that the availability of the experimental data will encourage others to make the further calculations required for a complete comparison.

In this paper we report data only for gaseous nitrogen compounds. Although many successful correlations and estimations have been made by using chemical shift data for solid compounds, there are both experimental and theoretical reasons for preferring the study of gaseous compounds. For example, by use of gaseous mixtures, it is a simple matter to measure chemical shifts between compounds of the same element from a single spectrum. Chemical shifts for gaseous compounds do not suffer from uncertainties of work functions which arise in the case of solid compounds.[1] Both theoretical and empirical calculations of core electron binding energies are much simpler for gaseous molecules than for solid compounds.

Experimental Section

Photoionization was accomplished with magnesium Kα X-radiation (1253.6 eV). An iron-free double-focusing magnetic spectrometer[13,14] was used to determine the kinetic energies of the photoelectrons. The gases were introduced from a metal vacuum line into a 200-ml source chamber. During each run, the pressure within this chamber was held constant (to ±20%) in the range 10–40 μ. First the pure compound was studied in order to determine the approximate magnitude of the photoelectron kinetic energy. Then an approximately 1:1 mixture of the compound and some convenient reference compound was studied. Nitrogen gas was the first choice as a reference because of its low reactivity, but other gases were used when the chemical shift was less than 2 eV from that of nitrogen gas. (Siegbahn, *et al.*,[6] have reported an absolute binding energy of 409.9 eV for N_2.) The width of each channel in the spectrum was 0.27 eV; the counting times were such that at least 1000 counts were recorded in the channel nearest the signal peak. The signal-to-noise ratios were in the range 4.0–8.7, and the widths of the photoelectron lines at half-height were in the range 1.0–1.5 eV. Most samples were run twice; we never observed a change in the chemical shift greater than 0.1 eV in different runs of the same compound. The spectrometer pressure was maintained at less than 10^{-4} μ.

Most of the gases were taken from commercial cylinders. Except for N_2, NO, N_2O, and NF_3, samples were purified by vacuum distillation. The purity of each sample was checked by mass spectrometry and by comparison of the infrared spectrum with the literature.[15–17] Hydrogen cyanide was prepared by the addition of potassium cyanide to phosphoric acid in a closed system. Its mass and infrared spectra agreed with the literature.[15–17] Dr. William Fox of Allied Chemical Co. kindly provided us with a sample of ONF_3.

Results and Discussion

The measured nitrogen 1s binding energies, relative to molecular nitrogen, are given in Table I. The values span a total range of 12.3 eV. In the following paragraphs we discuss these values in terms of the various methods of estimating chemical shifts in binding energies.

TABLE I
NITROGEN 1s BINDING ENERGIES FOR SOME GASEOUS COMPOUNDS

No.	Molecule	Rel binding energy, eV	Pauling atomic change	CNDO atomic change	Thermo estd rel energy, eV
1	ONF_3	7.1	1.24	0.70	
2	NF_3	4.3	0.45	0.30	
3	NO_2	3.0[a]	0.53	0.41	3.3[c,d]
4	$N\overset{*}{N}O$	2.6[a]	0.51	0.52	
5	N_2F_4	2.4	0.32	0.23	2.8[d–f]
6	ONCl	1.5	0.05	0.17	
7	NO	0.8[a,b]	−0.37	0.05	0.9[c,d]
8	N_2	0.0	0.00	0.00	0.0
9	$\overset{*}{N}NO$	−1.3[a]	−0.34	−0.24	−0.9[c,d]
10	HCN	−3.1	−0.06	−0.10	−2.6[c,d,g]
11	N_2H_4	−3.8	−0.26	−0.14	
12	NH_3	−4.3[a]	−0.39	−0.26	−3.5[c,d,h,i]
13	CH_3NH_2	−4.8	−0.32	−0.21	−3.9[c,d,i]
14	$(CH_3)_2NH$	−5.0	−0.23	−0.17	−4.2[c,d,j]
15	$(CH_3)_3N$	−5.2	−0.15	−0.14	

[a] The following values were obtained by Siegbahn, *et al.*:[6] NO_2, 2.99; $N\overset{*}{N}O$, 2.6; NO, 0.4; $\overset{*}{N}NO$, −1.4; NH_3, −4.3. [b] Weighted average of two peaks caused by spin of molecules. [c] U. S. National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952. [d] Document No. NSRDS-NBS 26, National Standard Reference Data System, U. S. National Bureau of Standards, Washington, D. C., June 1969. [e] A. Kennedy and C. B. Colburn, *J. Chem. Phys.*, **35**, 1892 (1961). [f] Calculated for the reaction $NF_2 + NO^+ \rightarrow OF_2^+ + N_2$. In view of the low dissociation energy of N_2F_4, this approximation is reasonable. [g] H. Pritchard and A. G. Harrison, *J. Chem. Phys.*, **48**, 2827 (1968). [h] M. A. Haney and J. L. Franklin, *ibid.*, **50**, 2028 (1969); J. L. Beauchamp and S. E. Buttrill, *ibid.*, **48**, 1783 (1968). [i] V. L. Tal'rose, *Pure Appl. Chem.*, **5**, 455 (1962). [j] The proton affinity of $(CH_3)_2O$ was estimated to be 190 kcal/mol on the basis of data given by M. S. B. Munson, *J. Amer. Chem. Soc.*, **87**, 2332 (1965).

Atomic Charge Method.—Previous studies of the relation between binding energies of solids and calculated atomic charges have shown improvement in the correlations when more sophisticated methods for calculating atomic charges were used.[2–5] The present binding energies for gaseous molecules should permit a more

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(10) H. Basch and L. C. Snyder, *Chem. Phys. Lett.*, **3**, 333 (1969).

(11) D. W. Davis, J. M. Hollander, D. A. Shirley, and T. D. Thomas, *J. Chem. Phys.*, **52**, 3295 (1970).

(12) M. Barber and D. T. Clark, *Chem. Commun.*, 22 (1970).

(13) J. M. Hollander, M. D. Holtz, T. Novakov, and R. L. Graham, *Ark. Fysik*, **28**, 375 (1965).

(14) T. Yamazaki and J. M. Hollander, *Nucl. Phys.*, **84**, 505 (1966).

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(17) For all others: R. H. Pierson, A. N. Fletcher, and E. S. Gantz, *Anal. Chem.*, **28**, 1218 (1956).

meaningful comparison of the correlating abilities of atomic charges calculated by different methods. Therefore in this study we have used both the Pauling and CNDO methods for calculating atomic charges.

The Pauling method is based on the relation between the ionic character of a bond and the difference in the electronegativities of the atoms.[18] We used Pauling's technique[19] for estimating the electronegativities of charged atoms and iterated the calculations until consistent sets of charges and electronegativities were obtained. For NO and NO_2, Linnett structures were used to establish the initial formal charges.[20] For N_2O, we used the average charges calculated from the initial structures $N^-{=}N^+{=}O$ and $N{\equiv}N^+{-}O^-$. The calculated Pauling charges are listed in the fourth column of Table I, and Figure 1 is a plot of binding energy *vs.* calculated charge. The least-squares-fitted straight line, $E_B = 7.45q - 0.87$, fits the points rather poorly, with an average error of ±1.62 eV.

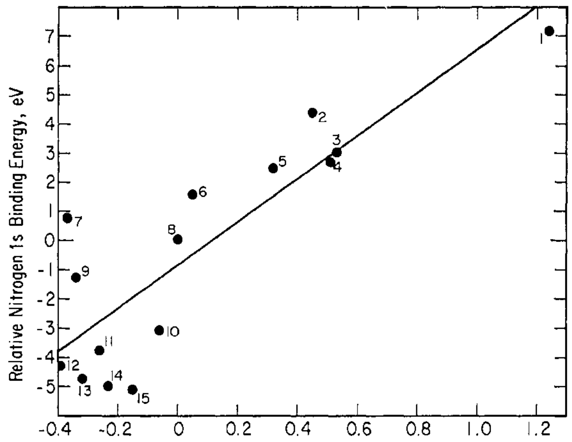

Figure 1.—Correlation of binding energy with atomic charge calculated by the Pauling method. Numbers refer to the compounds in Table I.

The CNDO molecular orbital calculations were made with a CDC 6400 computer using a Fortran IV program.[21] Cartesian coordinates were obtained from program PROXYZ[22] coupled with literature values of the molecular parameters.[23-25] The calculated CNDO charges are listed in the fifth column of Table I, and Figure 2 is a plot of binding energy *vs.* calculated charge. The least-squares-fitted straight line, $E_B = 11.83q - 1.27$, fits the points slightly better than the line in Figure 1, with an average error of ±1.26 eV.

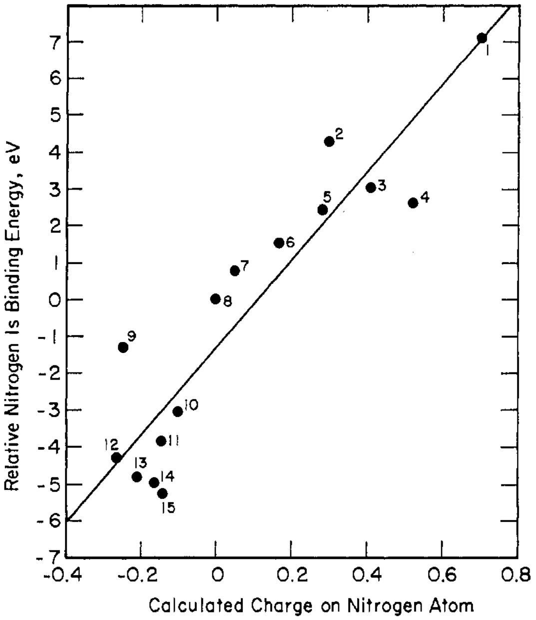

Figure 2.—Correlation of binding energy with atomic charge calculated by the CNDO method. Numbers refer to the compounds in Table I.

van der Avoird[26] has pointed out that the linear relationship between binding energies and atomic charges can be improved if the interatomic Madelung potential, M, is taken into account. We have confirmed this improvement. Using the Pauling charges, the least-squares line is $E_B - M = 18.08q - 0.95$, with an average deviation of ±1.40 eV. Using the CNDO charges, the least-squares line is $E_B - M = 23.97q - 1.62$, with an average deviation of ±0.99 eV.

Thermodynamic Method.—The difference in the nitrogen 1s binding energies of NH_3 and N_2 is the energy of the reaction

$$NH_3 + N_2^{+*} \longrightarrow NH_3^{+*} + N_2 \qquad (1)$$

$$\Delta E = E_B(NH_3) - E_B(N_2)$$

(The asterisks indicate 1s electron vacancies.) If we make the approximation that $\Delta E = 0$ for any process in which an N^{6+} core in one species is interchanged with an O^{6+} core in another species, we may write

$$NH_3^{+*} + NO^+ \longrightarrow OH_3^+ + N_2^{+*} \qquad (2)$$

$$\Delta E = 0$$

Then, by adding reactions 1 and 2, we obtain

$$NH_3 + NO^+ \longrightarrow OH_3^+ + N_2 \qquad (3)$$

$$\Delta E = E_B(NH_3) - E_B(N_2)$$

Thus the shift in binding energy is, to the accuracy of our approximation, equal to the energy of eq 3—a quantity which can be evaluated from available thermodynamic data. Similarly, most of the other chemical shifts in Table I can be approximated by thermodynamic data. The thermodynamically estimated chemical shifts are listed in the fourth column of Table I. The average discrepancy between the experimental and estimated values is ±0.52 eV. The latter value

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(18) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(19) Reference 18, 2nd ed, 1940, pp 65–66.

(20) J. W. Linnett, "The Electronic Structure of Molecules," Wiley, New York, N. Y., 1964.

(21) P. J. Pople and D. S. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970. Original program modified for use on the 6400.

(22) P. M. Kuznesof, Program No. QCPE 94, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind., 1966.

(23) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 11** (1958); **No. 18**, Suppl (1965).

(24) D. R. Lide, Jr., and D. E. Mann, *J. Chem. Phys.*, **31**, 1129 (1959).

(25) E. G. Curtis, D. Pilipovich, and W. H. Maberly, *ibid.*, **46**, 2904 (1967).

(26) A. van der Avoird, *Chem. Commun.*, 727 (1970).

is artificially high because of the choice of N_2 as the reference compound. The *overall* average discrepancy is only 0.3 eV. Figure 3 is a plot of the experimental binding energy shifts *vs.* the estimated shifts.

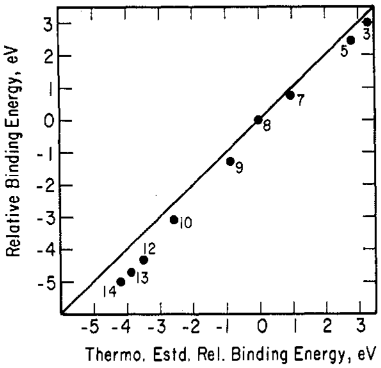

Figure 3.—Comparison of experimental and thermodynamically estimated binding energies. The line has a slope of unity and passes through the origin. The numbers refer to the compounds in Table I. The line would fit the points much more closely if point 9 or 10 (rather than 8) had been arbitrarily placed at the origin. It is significant that most of the points fit a line of unit slope.

Empirical Parameter Method.—It has been shown that chemical shifts in binding energy can be approximated by the sum of empirically evaluated parameters characteristic of the attached atoms or groups.[8] This additivity rule can be checked with a few of the binding energy data in Table I.

When all three hydrogen atoms of ammonia are replaced with methyl groups, the binding energy decreases by 0.9 eV. In the case of monomethylamine, the decrease would be expected to be one-third as much, 0.3 eV, whereas it is actually 0.5 eV. In the case of dimethylamine the predicted and actual decreases are 0.6 and 0.7 eV, respectively.

The addition of an oxygen atom to the nitrogen atom of NF_3 causes the binding energy to increase by 2.8 eV. (This is the chemical shift between NF_3 and ONF_3.) A similar change would be expected on adding an oxygen atom to molecular nitrogen. Indeed, the binding energy for the middle atom of N_2O is 2.6 eV greater than that of the atoms in N_2.

The binding energy of NF_3 is 8.6 eV greater than that of NH_3. We would expect the difference between N_2F_4 and N_2H_4 to be a little more than two-thirds as great, *i.e.*, a little greater than 5.73 eV. Indeed, the observed chemical shift between N_2F_4 and N_2H_4, 6.2 eV, is in agreement with this expectation. From the few comparisons made above, we tentatively conclude that the expirical parameter method is capable of predicting chemical shifts to about ±0.2 eV.

Computational Method.—Basch and Snyder[13] have obtained nitrogen 1s orbital energies for some of the compounds in Table I from SCF–MO calculations using a double-ζ basis of gaussian functions. According to Koopmans' theorem, these energies may be taken as equal to binding energies. Their calculated values, relative to N_2, are as follows (in eV): $\mathrm{N\overset{*}{N}O}$, 3.9; $\mathrm{\overset{*}{N}NO}$, 0.7; HCN, −2.4; N_2H_4, −3.8; NH_3, −5.4. The average deviation of these values from the experimental values is ±1.0 eV.

Conclusions

The Pauling atomic charge method, although it gives very rough correlations with binding energy, has the advantage that it can be applied to any set of molecules for which complete octet structures can be written. In the case of resonating molecules, ambiguity arises as to the relative weights of the resonance structures.[27] In these cases the experimental data can be used to establish the relative weights. Barber and Clark[12] cited the essentially equal carbon 1s binding energies of acetonitrile as evidence for the inadequacy of atomic charge–binding energy correlations. It is true, that by use of only the $H_3CC{\equiv}N$ structure, the CN carbon atom would be expected to have a significantly greater binding energy than the CH_3 carbon atom.[28] However contribution from the hyperconjugated $H^+H_2C{=}C{=}N^-$ structure (which cannot be ignored, in view of the observed acidity[29] of acetonitrile) would bring the carbon atom charges closer together, and thus the binding energy data are consistent with such hyperconjugation. Although the CNDO atomic charge method gives a slightly better correlation than the Pauling method, many chemists may consider this advantage to be outweighed by the relative difficulty and expense of the CNDO calculations.

The thermodynamic method gives more accurate predictions than the atomic charge method, and it is completely nonempirical, at least with respect to binding energies. However it is applicable only when the appropriate heats of formation are known or can be estimated.

The empirical parameter method has not yet been adequately tested with accurate gas-phase binding energy data. However, the few comparisons which we have been able to make indicate that, with the availability of appropriate sets of empirical data, the method should yield very accurate predictions.

Relatively few comparisons have been made between experimental and highly refined molecular orbital calculated binding energies. The available results show agreement to ±1 eV and suggest that the error due to the assumption of Koopmans' theorem is approximately the same for all molecules.[11]

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(27) For example, see the discussion of aniline in ref 6, p 121.

(28) The chemical shift between HCN and C_2H_6 is 2.8 eV.[11]

(29) R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, **75**, 2439 (1953).