Bonding and Valence Electron Distribution in Molecules.[1a] Experimental Binding Energies and Charge Distributions in Tetracyanoethylene, Tetracyanoethylene Oxide, Tetracyanocyclopropane, Cyclopropane, Ethylene Oxide, and Related Molecules

G. D. Stucky,*[1b] D. A. Matthews,[1b] J. Hedman,[1c] M. Klasson,[1c] and C. Nordling[1c]

Contribution from the School of Chemical Sciences, Department of Chemistry,
and Materials Research Laboratories, University of Illinois,
Urbana, Illinois 61801, and the Institute of Physics, University of Uppsala,
Uppsala, Sweden. *Received November 10, 1971*

Abstract: The applicability of the potential model for obtaining empirical charge distributions is examined for a number of small molecules which either contain only the elements carbon, nitrogen, and oxygen or the above elements and one other chemically unique atom. In the former case, the charge neutrality condition results in an overdetermined set of equations which relate atomic charge to binding energy, while, in the latter, the equations are solved exactly. An experimental value of the potential parameter k_N is obtained for nitrogen and the result applied to several nitrogen-containing compounds. It is observed that the binding energy is particularly sensitive to the charge distributions so that an empirical definition of atomic charge may be successful even though the model may not predict binding energies to better than 1 eV. The effect of ring substituents and ring atoms on the binding energies and charge distributions in three-membered rings is evaluated. Comparisons are made of the experimental charge distributions obtained with ESCA with those inferred from theoretical calculations (CNDO/2, INDO, and *ab initio*), quadrupole moments, X-ray–neutron diffraction experiments, and the chemistry of tetracyanoethylene oxide.

It has recently become apparent that combined X-ray–neutron diffraction data are capable of giving information concerning the aspherical charge distribution about atoms in molecules. The quantitative validity of the results which are obtained are, however, difficult to assess, and most evaluations of the diffraction results have been through comparisons with theoretical calculations, either with theoretical molecular scattering factors[2] or with semiempirical molecular orbital population statistics as described in the accompanying paper[1a] and in earlier work by Coppens[3] and Stewart.[4] An alternative approach is the comparison of the charge distributions obtained by the X-ray–neutron method with those of other techniques which give direct or indirect information about charge distributions in molecules. There are, however, only a very limited number of experimental methods which give such information. One example is the direct calculation of dipole and quadrupole moments from observed X-ray–neutron electron density distributions. Another technique is electron spectroscopy (ESCA), which has been demonstrated to be capable of giving information about charge distributions in molecules in a number of ways. It has been shown[5] that the relative shifts observed in the binding energies can be expected, to a good approximation, to be equal to the relative shifts in the quantum mechanical potential at the atomic 1s orbital. In principle, the latter is a function which can be calculated from diffraction data, since it is obtained from the expression

$$V(r_i) = -\int \rho(1)/r_{1i}\mathrm{d}\tau_1 + \sum_{\alpha}^{\text{nucl}}(Z_\alpha/r_{\alpha i})$$

where $\rho(1)$ is the monoelectronic density function and Z_α is the charge of nucleus α. In a more direct, but also more empirical approach, a large set of data obtained by measuring atomic core binding energies by electron spectroscopy has been used to estimate relative atomic charge distributions. One would hope that a basis could be found for comparison of these charges with those obtained from the population analysis of the diffraction data. Finally, recent observations[6,7] suggest that the cross section for the emission of a photoelectron from a given molecular orbital depends on the atomic character of that orbital. In the LCAO formalism, for example, molecular orbitals containing a large amount of carbon 2s character give stronger intensities than do those containing a large amount of 2p character.

In this paper, the results of the investigation by ESCA of a series of compounds, tetracyanoethylene (TCNE), tetracyanoethylene oxide (TCEO), tetracyanocyclopropane (TCCP), ethylene oxide (EO), and cyclopropane (CP), are described. The purpose of this work was fourfold: first, to provide a basis for comparison of the admittedly empirical charge distributions ob-

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[1] (a) The previous article in this series is by D. A. Matthews, G. D. Stucky, and P. Coppens, *J. Amer. Chem. Soc.*, **94**, 8001 (1972). This article is also one of a series of articles "Molecular Spectroscopy by Means of ESCA." The previous article in this series is ref 10 in the present paper. (b) University of Illinois; (c) University of Uppsala.

[2] D. S. Jones and W. N. Lipscomb, *Acta Crystallogr., Sect. A*, **26**, 196 (1970).

[3] P. Coppens, D. Paulter, and J. F. Griffin, *J. Amer. Chem. Soc.*, **93**, 1051 (1971), and included references.

[4] R. F. Stewart, *J. Chem. Phys.*, **53**, 205 (1970).

[5] M. E. Schwartz, *Chem. Phys. Lett.*, **6**, 631 (1970).

[6] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Heden, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, "ESCA Applied to Free Molecules," North-Holland Publishing Co., Amsterdam, 1969.

[7] U. Gelius, "Electron Spectroscopy," D. A. Shirley Ed., North-Holland Publishing Co., Amsterdam, 1972, p 311.

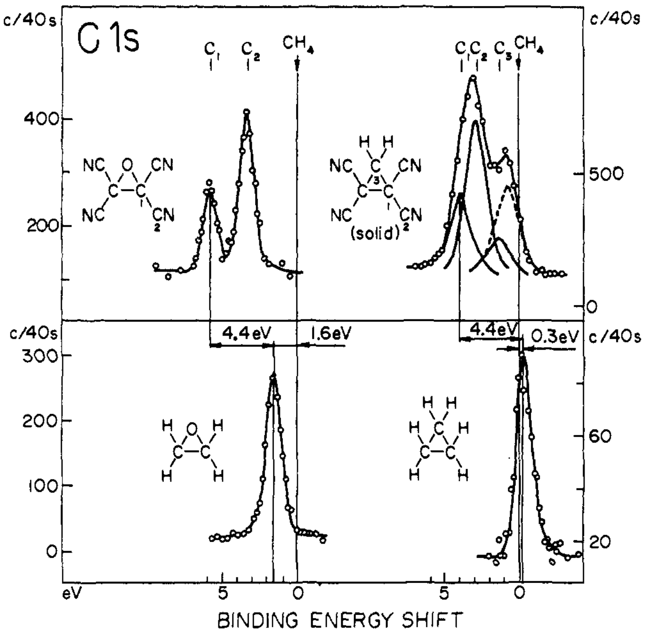

Figure 1.

tained by ESCA and the charge density analysis obtained with combined X-ray–neutron diffraction data; second, to determine if the gaseous and solid phase 1s binding energies had the same relative values within the experimental errors for the compounds TCEO and TCNE; third, to obtain values of the relative 1s binding energies for possible subsequent comparison with the quantum mechanical potential at the nuclei obtained from diffraction results; and finally, to investigate the effects of ring atoms (TCEO and TCCP) and ring substituents (TCEO and EO, TCCP and CP) in three-membered ring compounds on the atomic binding energies.

Experimental Section

Tetracyanoethylene oxide (TCEO) was prepared by Dr. Dave Matthews and Dr. J. S. Swanson by the method of Linn, Webster, and Benson[8] and then purified by sublimation before use. The sample of tetracyanocyclopropane (TCCP) was kindly supplied by Professor J. Hart of the Department of Chemistry of Michigan State University and was purified by slow recrystallization from ethanol. The remaining compounds were purchased as follows: tetracyanoethylene (TCNE), Eastman Organic Chemicals; ethylene oxide (EO), The Matheson Co.; cyclopropane (CP), Schuchardt.

The studies were made on an ESCA instrument[9] using a double focussing spectrometer for the spectral analysis of the photoelectrons. The characteristic Mg $K\alpha_{1,2}$ X-ray line, with an inherent width of approximately 0.7 eV, was used as excitant radiation. The obtainable resolution in the electron spectra is at present determined by the width of this line.

With the exception of TCCP, the samples were studied in the gas phase and were calibrated with core levels in methane, carbon dioxide, and nitrogen as energy standards. Carbon dioxide and methane have their C 1s levels 6.8 eV apart and the choice between these gases for the calibration of carbon spectra was determined by the wish to have a minimum interference between the calibration peak and the spectrum studied. The nitrogen spectra were calibrated against N 1s in N_2. In order to test the consistency in the calibration, carbon spectra in the nitrogen containing molecules were also calibrated against this level. No significant difference in the energies obtained with different calibration lines was found. The energies reported are supposed to be accurate within ± 0.2 eV.

TCNE and TCEO are both solids at room temperature. To obtain a sufficient vapor pressure in the collision chamber, a glass tube containing the samples, and its connection with the collision chamber, had to be heated to 40–60° during the measurements. Procedures of calibrating spectra from gaseous samples by mixing with a "standard" gas are further discussed in ref 6. It was not possible to obtain a vapor pressure high enough for measurements from TCCP, not even by heating the compound to 110°. It was therefore studied only in the solid state. TCNE and TCEO were studied in both the gas and solid phases. The spectrum from TCCP (Figure 1) which was recorded from the compound in the solid phase, contains a contribution from the hydrocarbon layer coating the sample surface in the spectrometer. In the solid phase spectra of TCNE and TCEO the position on the shift axis, corresponding to binding energy shift zero, appeared 0.9 eV to the right of the position of the peak from the hydrocarbon layer. With this position of the shift reference level the solid- and gas-phase spectra are comparable and the shifts for peaks from TCCP have been referred to this level. The deconvolution of complex spectra was made on a Du Pont 310 curve resolver.

Discussion

Binding Energies. The experimental results obtained for TCNE and TCEO show that, within the limits of the experimental resolution, the relative binding energies for a given molecule are the same in the gas phase as in the solid state. Owing to different definitions of the reference levels, there is a difference of about 6 eV between the binding energies for a solidified sample and for the same compound in the gaseous state. Similar observations have previously been made for a number of other organic compounds.[10] The fact that relative gas and solid phase shifts are observed to be the same does not of course exclude the possibilities that there are small differences well within the instrumental resolution or that some spatial polarization of valence electrons does occur. The latter in fact is highly probable, and, for example, differences in the valence state binding energies in the gas- and solid-state spectra of C_3O_2 have been observed.[11]

The observed binding energies (Figure 1 and Table I) for the cyanide groups show both expected and unexpected trends. The absolute values of the carbon and nitrogen binding energy shifts are essentially the same for TCNE and TCCP, but significantly different for TCEO. In addition, the 1s binding energy of nitrogen in TCEO is also different from that of either TCNE or TCCP. The substitution of the CH_2 group in TCCP for the isoelectronic oxygen atom in TCEO obviously has a pronounced effect on the properties of the nitrogen atom and the C≡N bond even though there are three intervening chemical bonds between the oxygen and nitrogen atoms in TCEO. This substitution also results in an increase in the binding energy of 1.9 eV for the ring carbon atom C_1. These results are of interest to the question of the transferrability of localized bonding properties among similar molecules and suggest that some caution is required.

The electron-withdrawing effect of the cyano groups is indicated by the comparison of the binding energies of TCEO with ethylene oxide, and TCCP with cyclopropane. The larger negative binding energy shift for oxygen in ethylene oxide (−4.5) compared to oxygen in

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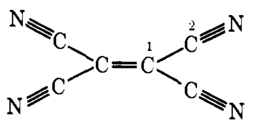
[8] W. J. Linn, O. W. Webster, and R. F. Benson, *J. Amer. Chem. Soc.*, 87, 652 (1965).

[9] R. Nordberg, J. Hedman, P. F. Heden, C. Nordling, and K. Siegbahn, *Ark. Fysik*, 37, 489 (1968).

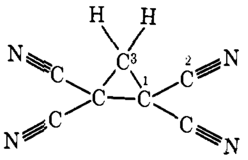
[10] U. Gelius, P. F. Heden, J. Hedman, B. J. Lindberg, R. Manne, R. Nordberg, C. Nordling, and K. Siegbahn, *Phys. Scr.*, 2, 70 (1970).

[11] U. Gelius, C. J. Allan, D. A. Allison, H. Siegbahn, and K. Siegbahn, *Chem. Phys. Lett.*, 11, 224 (1971).

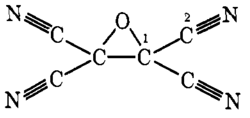
Table I. Observed 1s Core Binding Energies[a]



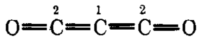
TCNE



TCCP

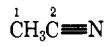


TCEO



$\overset{2}{\mathrm{O{=}C}}{=}\overset{1}{\mathrm{C}}{=}\overset{2}{\mathrm{C}}{=}\mathrm{O}$

C_3O_2



$\mathrm{\overset{1}{C}H_3\overset{2}{C}{\equiv}N}$

methyl cyanide

Compound	C_1	C_2	C_3	N	O
TCNE	4.0	3.1		−3.2	
TCEO	6.0	3.4		−2.8	−3.2
TCCP	4.1	3.1	1.4	−3.2	
Ethylene oxide	1.6				−4.5
Cyclopropane	−0.3				
CH_3CN[b]	2.1	2.1		−4.4	
C_3O_2[c]	0.8	4.2			−3.1
CO_2[d]	6.8				−2.3
N_2O[d]				−1.4, 2.6	−1.9
C_2H_4[d]	0.0				
C_2H_2[d]	0.4				
NH_3[d]				−4.3	
CS_2[d]	2.4				
CF_4[d]	11.1				
CCl_4[e]	5.5				
CBr_4[d]	3.9				
H_2O[d]					−3.4

[a] In eV, with carbon referred to CH_4 (290.7 eV), nitrogen to N_2 (409.9 eV), and oxygen to O_2 (543.1 eV), with numbering of the carbon atoms as shown. [b] Unpublished results. [c] Reference 11. [d] Reference 6. [e] T. D. Thomas, *J. Amer. Chem. Soc.*, **92**, 4184 (1970).

TCEO (−3.2) is consistent with this effect as are the relative ring carbon binding energies in these compounds and the corresponding carbon binding energies in TCCP (4.1) and cyclopropane (−0.3). The net effect is a binding energy increase for C_1 of 4.4 eV in TCCP and TCEO. The spectra in Figure 1 are discussed below in terms of calculated atom charges.

The Potential Model

The most successful empirical correlation between atomic charge distributions and core binding energies has been through the potential model[6,10] in which the chemical shift of an atomic level is given by

$$\Delta E = k_A q_i + V_i + l_A$$

where q_i = atomic charge, $V_i = \Sigma_{j\neq i}\, q_j/R_{ij}$, and k_A and l_A are constants for the studied type of atom. The approximations in this equation have been discussed by a number of investigators.[5,12–15] In particular, the quantum mechanical model from which the above expression is derived does not take into account energy terms due to the rearrangement of the electronic structure during inner shell ionization. This is not insignificant and has been estimated to be of the order of 10–20 eV.[16] In spite of this, the potential model has been used to fit binding energies to less than 1 eV, so that a major part of the rearrangement energy must be included in some fashion. Snyder[13] has suggested an expression for the reorganization of the 1s core-hole states of the form

$$E(\text{reorg}) = -1.2 - 2.5C_2 - 1.5C_3 \text{ eV}$$

where C_2 is the number of electrons with principal quantum number $n = 2$ and C_3 is the number of electrons with principal quantum number $n = 3$.

Consider the case where nitrogen 1s binding energies are measured relative to the nitrogen atom in N_2. With the reorganization energy term included, the potential model expression can be written as

$$\delta E(\text{M}) = q_i(\text{M})k'_A + V_i(\text{M}) + l_A + E(\text{reorg})$$

or for the nitrogen atom in N_2

$$\delta E_N(N_2) = l_N - 1.2 - 2.5C_2^N$$

For the observed energy shift for another molecule containing nitrogen, one has

$$\delta E_N(\text{mol}) = q_N k'_N + V_N(\text{mol}) + l_N - 1.2 - 2.5C_2^{\text{mol}}$$

Assume that the quantity C_2^{mol} is given by the gross atomic charge = $(5 - q_N)$ and that for N_2, $C_2^N = 5$. Then

$$\Delta E = \delta E_N(N_2) - \delta E_N(\text{mol}) = q_N k'_N + V_N(\text{mol}) + 2.5q_N = k_N q_N + V_N(\text{mol})$$

i.e., using Snyder's model the rearrangement energy is incorporated into the k parameter of the potential expression. The procedure previously followed[10] has been to determine k' from a fit of experimental shifts to those calculated from *ab initio* and semiempirical theoretical calculations. This method gives, in fact, a quantity k which takes into account most of the rearrangement energy. The experimental correlations with the potential model for a large number of carbon compounds and the theoretical calculations of Schwartz[5] for CH_4 and HCN both indicate that the reorganization energies of atoms in different molecular sites are quite similar.

In ref 10, the values of the parameters k and l were obtained from *ab initio* SCF calculations which give total energies close to the Hartree–Fock limit[10] and the observed 1s binding energies. A least-squares fit using the *ab initio* charges for CH_4,[17] CF_4,[10] and CO_2[10] (q_C = −0.156, 1.007, and 0.66, respectively) and the corresponding 1s binding energies gives values of k_C = 20.7 and l_C = 1.0. Similarly, it is found that k_0 = 26.0 using the experimental and theoretical data for CO_2[10] and O_2. The carbon 1s binding energies are referred to methane while the oxygen 1s binding energies are referred to O_2. Molecules without hydrogen atoms with well-separated core binding energies have the advantage that the potential model equations plus the neutrality requirement give one more observable quantity than there are unknown charges. This is the case for TCNE, TCEO, and C_3O_2, so that the dependencies of the charge parameters and l_C upon the coefficients k_C, k_N, and k_O for atoms in these molecules can be investigated. For example, the four equations

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(12) H. Basch, *Chem. Phys. Lett.*, **5**, 337 (1970).

(13) L. C. Snyder, *J. Chem. Phys.*, **55**, 95 (1971).

(14) F. O. Ellison and L. L. Larcom, *Chem. Phys. Lett.*, **10**, 580 (1971).

(15) M. E. Schwartz, J. D. Switalski, and R. F. Stronski in ref 7.

(16) M. E. Schwartz, *Chem. Phys. Lett.*, **5**, 51 (1970).

(17) B. Roos and P. Siegbahn, *Theor. Chim. Acta*, **17**, 199 (1970).

obtained from the potential model are given in (1) in matrix form for TCNE. The last equation is the con-

$$\begin{pmatrix} 10.97 + k_C & 31.93 & 19.56 & 1.0 \\ 15.97 & 14.80 + k_C & 23.95 & 1.0 \\ 9.78 & 23.95 & 9.31 + K_N & 0.0 \\ 2 & 4 & 4 & 0.0 \end{pmatrix} \times \begin{pmatrix} q_{C1} \\ q_{C2} \\ q_N \\ l_C \end{pmatrix} = \begin{pmatrix} 4.0 \\ 3.1 \\ -3.2 \\ 0.0 \end{pmatrix} \qquad (1)$$

dition of neutrality. Cyanide carbon atoms are labeled C2 and ethylenic carbon atoms, C1. l_C is treated as an unknown parameter, while $l_N = 0$ since the binding energy shifts for the nitrogen atoms are referred to N_2 in which the nitrogen atomic charge is defined as zero. The interatomic distances required for matrix elements are taken from the single crystal structural results reported for the monoclinic form of TCNE.[18]

Calculation of the Parameters k **and** l. A computer program was written which calculated values of the charges and the parameter l_C for incremented values of k_C and k_N. The range of values tried for k_C was between 18.0 and 23.0 eV/unit charge. The values of k_N were examined from $k = 18.0$ to 34.0 eV/unit charge. The charges and values of l_C proved to be smoothly varying quantities with increments of 1.0 in the values of k_N and k_C.

The C 1s binding energies were referred to that of carbon in methane (290.7 eV). The potential model expression and the electroneutrality condition then give for methane

$$l_C = -q_C k_C + 14.4\frac{q_C}{R_{C-H}} = -q_C\left(k_C - \frac{14.4}{R_{C-H}}\right)$$

where R_{C-H} is the distance in ångströms between the carbon atom and a hydrogen atom when l_C is expressed in electron volts. Since $k_C > 14.4/R_{C-H}$ and all theoretical calculations indicate that $q_C < 0$ for methane, the result is obtained that l_C is a positive quantity. This criterion excludes several combinations of k_C and k_N. For instance for $k_C > 18$, only $k_N \geq 24$ fulfills the criterion and for $k_C > 20$, $k_N > 26$ is required. The values of $k_C = 20.7$, $l_C = 1.0$, and $k_O = 26.0$ were found by analyses similar to that described for TCNE to give a good fit to the experimental binding energies for CO_2, C_3O_2, TCNE, and TCEO. From these values and the data for TCNE the value of k_N is determined to be approximately 31.0 eV/unit charge. This result also agrees with that given by the theoretical *ab initio* charge distribution for NH_3 (footnote *e* of Table II). The relative ordering of k's from CNDO/2 correlations[6] are $k_O > k_C > k_N$. The experimental data here indicate that the order is $k_N > k_O > k_C$. The constant k_i in the potential model is the first derivative of the core ionization potential with respect to the total number of valence electrons on atom i. The quantum mechanical interpretation of k_i is that it is approximately proportional to the electrostatic interaction integrals between the core orbital and electrons in molecular orbitals which have a significant probability of being at the atomic site.[10,12,13] This includes primarily the other valence atomic orbitals in the same atom. The trend $k_N > k_O > k_C$ is similar to that observed for valence ionization potentials, which can be explained in terms of correlation effects.[19]

An examination of the potential equations for N_2O was also made for all integral combinations of k_N and k_O in the ranges $19.0 < k_N < 34.0$ and $19.0 < k_O < 34.0$. l_N was set equal to l_O and treated as an unknown parameter. Since the binding energies of the nitrogen and oxygen atoms in N_2O are referred to N_2 and O_2, the potential model requires that $l_N = l_O = 0$. In fact, there was *no* combination of k_N and k_O for which this was true with the difference in the calculated and observed binding energies being in the range 0.6 to 1.0 eV, ΔE(obsd) < ΔE(calcd). A value of $k_N = 23.4$ which is intermediate between that of $k_O = 26.0$ and $k_C = 20.7$ gives $q_N = -0.16$ (terminal nitrogen) and $q_O = -0.15$. The *ab initio* calculations of Basch and Snyder[20] and CNDO/2 calculations give $q_N < q_O$. The atomic charges given by the potential model for $k_N = 31.0$ and $k_O = 26.0$ are $q_N = -0.07$ and $q_O = -0.11$, which agrees with the expected ordering of these charges. The potential model also predicts the 1s binding energies to be as much as 0.4 eV too small in C_3O_2.

There are several observations which can be made at this point concerning the potential model. One of the purposes of this study was to use this model to *experimentally* obtain a set of empirically defined atomic charges. If the success of this attempt is measured by the fit of the calculated to the observed binding energies, a very good correlation (deviations less than 0.3 eV) can be obtained for molecules which contain only saturated bonds or multiple bonds involving two heteroatoms. A much poorer fit is obtained for molecules which are legitimately described by more than one valence bond structure (N_2O) or which contain delocalized bonds with the same atoms as do the central carbon atom in C_3O_2 or the carbon atoms in benzene. Both types of systems are obviously not well defined except in a molecular orbital sense and are not suitable candidates for the localized atom approximations inherent in the potential model. Secondly, an interesting suggestion has been made recently[14] that the function of Coulomb and exchange integrals represented by k might be quite different for 2s and 2p parameters. It is then necessary to redefine the potential equation in terms of a two-parameter instead of a one-parameter model. It would be interesting to determine if this model with empirically determined parameters will also correctly take into account binding energies in molecules in which the reorganization energies are significantly different from that in the reference compound. Finally, small variations in atomic charge (~0.05 electron) give relatively large changes in binding energies. For example, if the neutrality condition for the molecule is eliminated, the experimental 1s binding energies of N_2O are fit *exactly* by the set of charges q_N(terminal) = -0.09, q_N(inner) = 0.17, and $q_O = -0.13$. Yet core charges calculated for N_2O

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[18] D. A. Bekoe and K. N. Trueblood, *Z. Kristallogr.*, **113**, 1 (1960).

[19] J. C. Slater, "Quantum Theory of Atomic Structure," Vol. 1, McGraw-Hill, New York, N. Y., 1960.

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

with the neutrality condition (q_N(terminal) = −0.07, q_N(inner) = 0.18, and q_O = −0.11) give binding energies which are off by 1.0 eV for oxygen and 0.8 eV for N(terminal). This sensitivity of binding energy to charge suggests that the empirical definition of atomic charge may be successful even though binding energies are not reproduced to better than 1.0 eV.

Determination of Atomic Charges. In order to determine the atomic charges for TCNE, TCEO, CO_2, C_3O_2, and N_2O, the neutrality equation was again treated as an observation, but with the potential model parameters set at $k_N = 31.0$, $k_C = 20.7$, $l_C = 1.0$, and $k_O = 26.0$. The neutrality constraint was fit exactly by using it to solve for one of the atomic charges in terms of the other charges and substituting the result in all the other equations. These equations were then solved by standard linear least-squares procedures. The errors in the atomic charges were estimated by the following expression

$$\sigma(q_k) = (A^{kk})^{1/2}\sigma$$

where A^{kk} = the diagonal elements of the inverse matrix of the normal equations and

$$\sigma^2 = \frac{1}{n - m}\sum(\Delta E_i^{\text{obsd}} - \Delta E_i^{\text{calcd}})^2$$

n = number of observational equations, m = number of unknown parameters, ΔE_i^{obsd} = observed binding energy shift, and $\Delta E_i^{\text{calcd}}$ = calculated binding energy shift. The errors were also calculated using the estimated error in the observed binding energies, and in all cases the larger error was used. A summary of the results is given in Table II. A number of compounds for which binding energies have been previously measured and which seemed relevant to the present study were also included. For those compounds which contain one chemically unique atom besides carbon or nitrogen, the charges were obtained by solving the potential and neutrality equations exactly. Since there are as many equations as unknowns for these systems, the energies are fit exactly.

The charge distributions obtained by ESCA with few exceptions are consistent with those calculated by theoretical methods. Thus in every case $|q_C| < |q_N|$ for the cyanide groups with the magnitudes of the differences being comparable to those predicted by CNDO/2 calculations. The change in binding energy primarily reflects the change in the quantum mechanical potential at the 1s orbital, and it is significant that while the charges on the nitrogen atoms are nearly constant, the binding energy for the cyanide nitrogen atom in TCNE is 0.4 eV greater than that for the corresponding atom in TCCP. This difference is due to changes in the contribution of other atomic centers to the nitrogen 1s potential. In this connection it should be noted that the C–C(ring) bond length is 1.496 (2) Å in TCEO[21] and 1.559 (4) Å in TCCP.[22] When this work was first initiated, the structural parameters for TCCP were not available and the geometry for this molecule was assumed to be that obtained by superimposing $(CN)_2C{-}C(CN)_2$ fragment from TCEO with the C–C(ring) distances of cyclopropane. CNDO/2 calculations give a total valence electron energy of −2799.38 eV compared with −2799.85 eV for the true configuration. The charge distributions for the atoms were also considerably different: $q(C_1) = 0.14$, $q(C_2) = -0.05$, $q(C_3) = 0.15$, $q(N) = -0.23$, and $q(H) = 0.05$. It has been suggested that bond electron density distributions may be transferrable from molecule to molecule; for example, the theoretical calcula-

Table II. Charges Obtained from Observed 1s Binding Energy Shifts and from Semiempirical Calculations

Compd	Atom[a]	ΔE = ΔE_i(obsd) − ΔE_i(calcd), eV	q_i	q_i(CNDO/2)	
TCNE	C_1	0.0	0.04 (1)	0.05	
	C_2	0.0	0.17 (1)	0.11	
	N	0.0	−0.19 (1)	−0.14	
TCEO	C_1	0.0	0.25 (1)	0.16	0.18[b]
	C_2	0.0	0.12 (1)	0.09	0.09[b]
	N	0.0	−0.17 (1)	−0.12	−0.13[b]
	O	0.0	−0.33 (1)	−0.18	−0.20[b]
TCCP	C_1		0.08	0.04	
	C_2		−0.13	0.00	
	C_3		0.16	0.11	
	N		−0.19	−0.15	
	H		0.03	0.04	
EO	C_1		0.06	0.10	
	O		−0.25	−0.21	
	H		0.03	0.00	
CP	C_1		−0.10	−0.02	
	H		0.05	0.01	
CH_3CN[f]	C_1		0.01	−0.02	
	C_2		0.16	0.09	
	N		−0.20	−0.16	
	H		0.01	0.03	
C_2H_4[f]	C		−0.08	−0.03	
	H		0.04	+0.02	
CO_2[f]	C_1	0.1	0.68 (3)	0.54	0.66[c]
	O	0.2	−0.34 (3)	−0.27	−0.33[c]
C_3O_2	C_1	−0.2	−0.33 (3)	−0.56	−0.60[d]
	C_2	−0.3	0.45 (6)	0.56	0.59[d]
	O	−0.4	−0.29 (3)	−0.29	−0.25[d]
N_2O	N_1	−0.8	−0.07 (7)	−0.18	
	N_2	−0.5	0.16 (7)	0.52	
	O	−1.0	−0.10 (6)	−0.34	
NH_3[e,f]	N		−0.26	−0.25	
	H		0.09	0.08	
CS_2	C		0.12	0.25	
	S		−0.06	−0.12	
CF_4	C		1.02	0.85	1.00[c]
	F		−0.25	−0.21	−0.25[c]
CCl_4	C		0.36	0.35	0.48[g]
	Cl		−0.09	−0.09	−0.12[g]
CBr_4	C		0.21		0.20[g]
	Br		−0.05		−0.05[g]
H_2O[e,f]	O		−0.31	−0.28	
	H		0.15	0.14	
C_2H_2[f]	C		−0.05	−0.06	
	H		0.05	0.06	

[a] See Table I for numbering of atoms. [b] INDO results as reported by D. A. Matthews, G. D. Stucky, and P. Coppens, *J. Amer. Chem. Soc.*, **94**, 8001 (1972). [c] *Ab initio* charges from ref 6. [d] *Ab initio* charges from ref 1. [e] The *ab initio* charge for the nitrogen atom in NH_3 is reported[7] as −0.22 for a basis set including p orbitals on hydrogen atoms but no d orbitals on nitrogen and −0.30 for the same basis set but including d orbitals on nitrogen. The corresponding values for H_2O are −0.28 and −0.34. The value of the potential parameter, k, calculated from these *ab initio* values and the observed shifts for N_2 and O_2 are k_n = 33.8, 28.5, and k_O = 27.2, 25.0. [f] CNDO/2 values taken from J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970. [g] Atomic charges obtained from quadrupole coupling data as described in ref 27.

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(21) D. Matthews, J. Swanson, M. Mueller, and G. D. Stucky, *J. Amer. Chem. Soc.*, 93, 5945 (1971).

(22) Y. Wang and G. D. Stucky, unpublished results.

Table III. Charges Derived from Diffraction and ESCA Data and from Semiempirical Calculations

TCEO	Spherical atom STO ELS[b]	DA[c]	1-Center[a] STO[d]	ESCA	INDO	CNDO
O	−0.05 (2)	−0.12 (2)	−0.19	−0.33	−0.20	−0.18
C(1)	−0.04 (3)	−0.13 (4)	0.04	0.12	0.09	0.09
C(2)	0.02 (3)	0.02 (4)	0.07	0.12	0.09	0.09
C(3)	−0.15 (2)	−0.01 (3)	−0.18	0.12	0.09	0.09
C(4)	0.05 (3)	0.16 (4)	0.06	0.12	0.09	0.09
C(5)	−0.06 (2)	−0.15 (2)	0.09	0.25	0.13	0.16
C(6)	−0.10 (2)	−0.10 (3)	0.09	0.25	0.13	0.16
N(1)	0.05 (2)	0.16 (4)	−0.03	−0.17	−0.13	−0.12
N(2)	0.06 (2)	0.16 (4)	−0.01	−0.17	−0.13	−0.12
N(3)	0.15 (2)	0.11 (4)	0.11	−0.17	−0.13	−0.12
N(4)	0.07 (3)	−0.03 (4)	−0.05	−0.17	−0.13	−0.12
TCNE[e]						
C(1)	0.20 (2)			0.04		0.05
C(2)	−0.09 (3)			0.17		0.11
N	−0.01 (3)			−0.19		−0.14
TCNE–Perylene[e]						
C(1)	0.04 (3)					
C(2)	0.04 (5)					
C(2)	0.11 (5)					
N	−0.04 (5)					
N	−0.02 (5)					

[a] 1-center = one-center refinement. [b] STO = Slater type orbital basis set, ELS = extended L-shell projection. [c] DA = double atom refinement. [d] X-Ray refinement data and INDO results as reported in ref 26. Note cyanide carbon atoms are numbered C(1)–C(4). [e] R. G. Little, D. Paluter, and P. Coppens, *Acta Crystallogr.*, submitted for publication.

tions of McLean and Yoshimine,[23] have been used to demonstrate this for the $C\equiv C$ bond in $LiC\equiv CH$ and $HC\equiv CH$.[24] Clearly, substitution on the ring carbon atoms in TCEO and TCCP results not only in a different charge distribution (see below), but a different C–C geometry as well. Replacing the CH_2 group in TCCP with the more electronegative oxygen atom in TCEO results in an increase in the positive charges on the cyanide and ring carbon atoms of 0.04 and 0.16, respectively. The difference in charges for the ring carbon atoms in EO and CP (0.16) is gratifyingly similar to that found for TCEO and TCCP (0.17). Replacing hydrogen atoms by cyanide groups (EO and TCEO, CP and TCCP, ethylene and TCNE) also gives a relatively constant change in the ethylene carbon charges (0.19, 0.18, and 0.16, respectively). This substitution apparently affects the carbon charges only slightly more than replacing the ring CH_2 group with an oxygen atom. This result is also evident in the macroscopic physical properties of TCEO and TCNE. TCEO is a volatile and easily sublimable material with a measured dipole moment of less than 0.2 D. TCCP is nonvolatile, cannot be sublimed, and has a dipole moment of approximately 2.0 D. The component of the dipolar moment due to the oxygen atom is slightly more than compensated by the component of the dipole moment due to the cyano groups in TCEO. The experimental dipole moment of ethylene oxide, of 1.88 D, is less than that of TCCP and is in agreement with this.

Comparison with Charge Distributions Inferred from Other Techniques and the Chemistry of TCEO

A number of attempts to measure valence electron distributions in molecules have been made during the past few years using diffraction techniques. The procedure which gives the maximum amount of information requires the use of both neutron and X-ray diffraction data. The thermal motion of the atoms and the average nuclear positions are determined from the neutron refinement. The free atom and molecular electron densities can then be compared by difference Fourier techniques in which the electron density calculated from free spherical atom distributions convoluted into the thermal motion of the atom in the actual molecule is subtracted from the observed X-ray electron density. The difference electron distributions which have been obtained by this technique are consistent with qualitative notions of how electron distributions should behave in molecules. For example, in TCEO electron distributions due to lone-pair electron densities on oxygen and cyanide atoms and the "bent" bonds in the three-membered ring are clearly evident. Unfortunately, the above approach does not lend itself to results which can be directly compared with information about molecular charge distributions obtained by other techniques, such as dipole and quadrupole moments. Coppens[3] and Stewart[4] have suggested refinement of charge distribution *via* an expansion in terms of the first-order density matrix. The basis functions in this case are the atomic functions, either Slater or Hartree–Fock, commonly used in quantum mechanical calculations. A more primitive method, but one which is easier to apply, is to consider the valence and core electron distributions to be spherical but the number of electrons in the valence shell to be variable. The centers of the core and valence distributions can be refined independently.[3,4,25] The diffraction results for the molecules TCNE[3] and TCEO[26] as well as comparison with the ESCA results obtained here are given in Table III.

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(23) A. D. McLean and M. Yoshimine, IBM *J. Res. and Develop.*, 11, 1 (1967). Tables of Linear Molecular Wave Functions.

(24) F. L. Hirchfeld, International Symposium on Crystal Structure and Chemical Bonding, Enschede, Netherlands, Aug 1971.

(25) P. Coppens, *Acta Crystallogr*, submitted for publication.

(26) See P. Coppens, G. D. Stucky, and D. Matthews, in ref 1a.

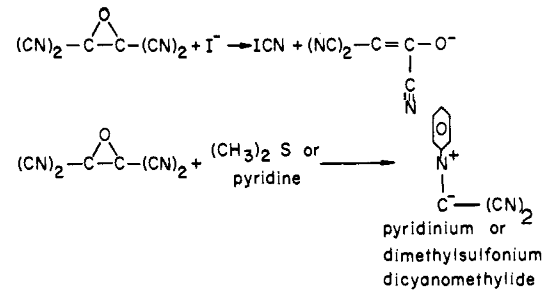


Figure 2. Reaction of TCEO with I$^-$, $(CH_3)_2S$, and pyridine.[28]

Excluding one cyano group, C(3)–N(3), the diffraction charge analysis obtained with the one-center refinement of TCEO gives good agreement between chemically equivalent, but crystallographically nonequivalent portions of the molecule. Also encouraging is the fact that the relative carbon atom charges on the ring and cyano carbon atoms are consistent in the ESCA and one-center diffraction methods, with q_C(cyano) > q_C(ring).

The ESCA, CNDO, and INDO results indicate that the charge distribution as described by the spherical atoms has resulted in too much electron density on the ring and cyano carbon atoms at the expense of the cyano nitrogen atoms. The same is true to a lesser extent of the one-center refinement in that the net charge on the cyano groups is >0, a chemically unsatisfying result. The same results are evident in the diffraction data for TCNE and TCNE–perylene. Only the refinement of two-center density matrix coefficients accounts explicitly for charge density in bonding regions and gives a good fit to the experimental difference electron distribution determined using X-ray and neutron data. The results for this type of calculation for TCEO are presented in ref 26 where the average net charge for the cyano group was found to be −0.10. In spite of the fact that 1s binding energies are primarily functions of the potential at the 1s orbital, while the diffraction experiment is more sensitive to valence electron distributions, the limited data which are now available suggest that the atomic charge which is empirically defined by the two experiments will be reasonably consistent in the limit at the two-center refinement of the diffraction data. The ESCA results as well as the difference maps of ref 26 clearly point out the need for the inclusion of two-center density matrix coefficients in order to reproduce the experimental diffraction data and obtain a realistic description of the charge distribution. It would also appear that low-temperature (liquid helium) diffraction data may be required for most molecules.

There is good agreement between the atomic charge distributions for CCl_4 and CBr_4 as estimated from quadrupole coupling constants by Gordy[27] and those determined from the ESCA data and the potential model. The values obtained by Gordy are −0.12 electron for the chlorine atom in CCl_4 and −0.05 electron for the bromine atom in CBr_4. The corresponding ESCA values are −0.09 and −0.05 electron (Table II).

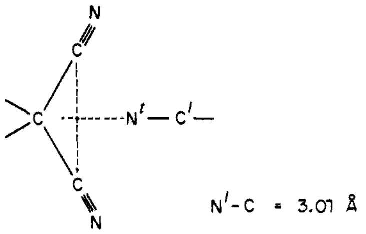
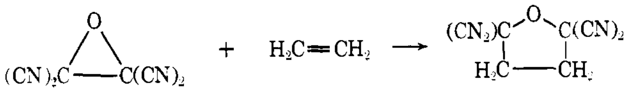


Figure 3. Packing of TCEO cyano-nitrogen atoms in the solid state.[21]

The chemistry of TCEO is consistent with the one- and two-center diffraction and ESCA results. TCEO does not undergo ring opening on electrophilic attack as do most three-membered ring systems.[28] Instead, it undergoes nucleophilic attack as shown in the reactions in Figure 2. The charge distributions obtained for TCEO are consistent with the formation of an intermediate species which consists of an acid–base adduct with the active site of the base interacting with the triangle defined by two adjacent cyano carbon atoms and the attached ring carbon atom. This configuration is observed in the solid state for TCEO[21] (Figure 3) where the base is the cyano nitrogen atom of an adjacent TCEO molecule. The products of the reactions in Figure 2 are what one would expect from the formation of intermediates of this type.

A second type of reaction of interest is that of TCEO with ethylene.[28]



The kinetics of this thermal reaction indicate the formation of an activated TCEO species and the subsequent concerted addition of ethylene. The observed polarization of charge in TCEO favors this reaction, first by the large concentration of positive charge on adjacent ethylenic carbons (+0.25) which weakens the C–C bond (1.496 Å in TCEO, 1.470 Å in EO) and secondly again through what can be considered an acid–base reaction in which the ethylene molecule carbon atoms behave as nucleophiles (q_C = −0.10) toward the electropositive regions near the TCEO carbon atoms.

Acknowledgment. This work has been supported by the Swedish Natural Science Research Council and by The Advanced Research Projects Agency under Contract HC 15-67 CO221. Helpful discussions with Dr. U. Gelius are also appreciated. One of the authors, G. S., would particularly like to express his appreciation to K. Siegbahn and C. Nordling for the warm hospitality and use of equipment during his stay at Uppsala University.

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(27) W. Gordy, *Discuss. Faraday Soc.*, **19**, 14 (1955).

(28) W. J. Linn, O. W. Webster, and R. E. Benson, *J. Amer. Chem. Soc.*, **87**, 3647 (1965).