Charge Distribution on the Cyanide Ion and Cohesive Energies of Sodium and Potassium Cyanides

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The charge distribution on the cyanide ion has been studied by molecular-orbital calculations. The probable charges on the carbon and nitrogen atoms in $[CN]^-$ are −0.40 and −0.60 electron units, respectively. The results have been used in evaluating the cohesive energies, on an electrostatic model, of two polymorphs of sodium and potassium cyanides. A value of -379 kJ mol^{-1} is obtained for the electron affinity of the CN species.

CALCULATIONS of cohesive energies of ionic solids involving polyatomic ions, using a point-charge model in which the charges are considered to lie at the centres of ions or groups of ions, are well known.[1,2] Alternatively, a distributed-charge model may be employed, in which account is taken of the fractions of the total charge of a polyatomic ion which may be considered to reside on the individual atomic centres in the ion. In some compounds, charge distributions have been determined from energy relations among polymorphs.[3-6] However, it is sometimes difficult to judge the reliability of such calculations as, frequently, no independent method of assessing the same parameters has been used.

Some estimates of charge distributions have been made by theoretical calculations. In the carbonate ion, good agreement between two methods was obtained.[7] However, for the cyanide ion such agreement was poor, and in an earlier paper [3] the energetic approach was preferred: the results from the theoretical calculation were at variance with the relative electronegativities of the C and N species, and were not reported at that time. This paper considers energy calculations for ionic solids containing polyatomic ions, with particular reference to alkali-metal cyanides.

CALCULATIONS

Charge Distribution on the Cyanide Ion.—The CNDO/2 and INDO molecular-orbital (m.o.) methods have been discussed in detail.[8,9] Here, calculations were made for different interatomic distances in the $[CN]^-$ ion, finding both the charges on the species and the total energy for each geometry. Similar calculations were made on the CN species in the hope that the difference in the minimum total energy between $[CN]^-$ and CN could be correlated with the electron affinity of CN. Further sets of these calculations have been carried out by an *ab initio* m.o. method.[10-12] A Mulliken population analysis was also performed.

Some results are illustrated in Figure 1. Reasonable values for z_N and z_C,* judged both in terms of their relative electronegativities and the results reported later in this paper, are −0.60 and −0.40: since *ab initio* calculations tend to give high values for dipole moments, the lower value for z_N was chosen.

Electrostatic Energy.—In calculating the electrostatic energy of an ionic solid with a view to relating it to thermodynamic parameters, it is necessary to take account of the appropriate reference energy levels. In point-charge models there are no complications, but in distributed-charge models the self energy of the polyatomic ion must be included. This situation can be appreciated readily by reference to Figure 2.

In a point-charge model the self-energy term is zero, and the total electrostatic component of the cohesive energy resides in the Madelung energy. In a distributed-charge model, however, the self energy must be calculated and added algebraically to the Madelung energy, the sign of the addition depending on the signs of the individual charges in the complex ion, z_C and z_N in this work. From Figure 2 it is evident that the self energy is a property of the gaseous

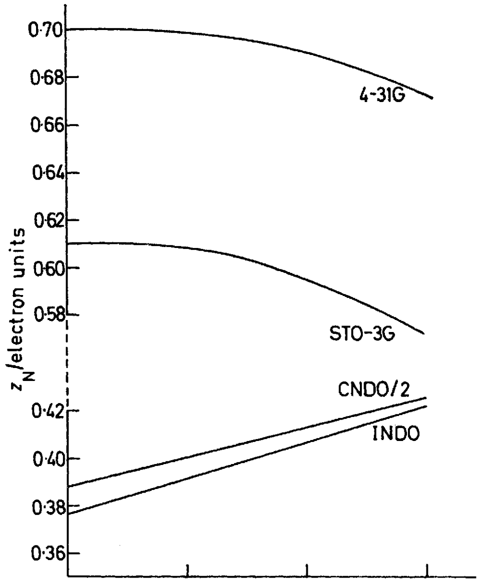

FIGURE 1 Variation of z_N with R for $[CN]^-$

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* For the meanings of the symbols used in this paper see the Appendix.

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[4] M. F. C. Ladd, *Nature (Phys. Sci.)*, 1972, **238**, 125.

[5] M. F. C. Ladd, *Theor. Chim. Acta*, 1972, **25**, 400.

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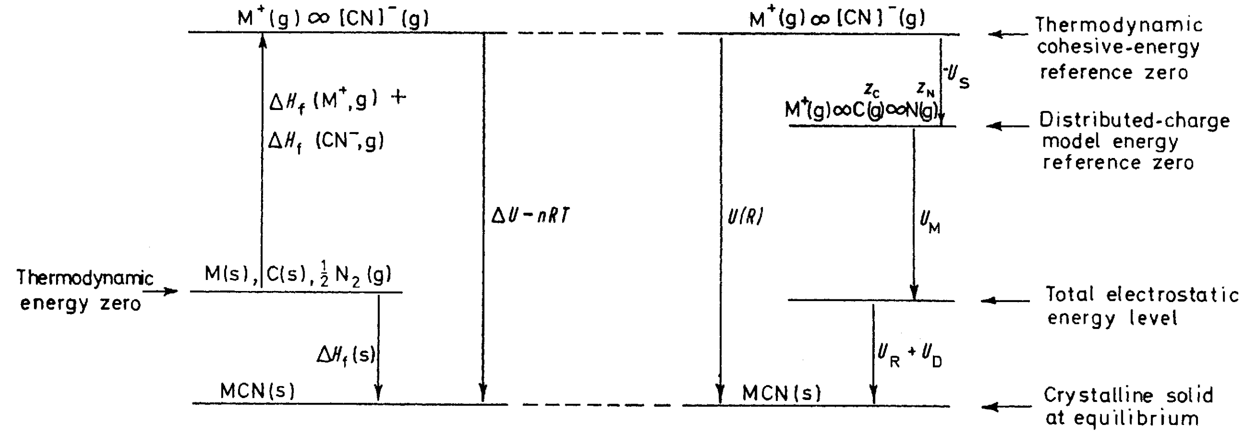

FIGURE 2 Energy relations for ionic solids; the broken lines separate the thermodynamic (left) and electrostatic models (right)

ion.[6] However, in order to take account of its geometry in the structure, the self energy is calculated from the value of the C–N interatomic distance r in the crystal, and charges z_C and z_N appropriate to this distance ($z_C + z_N = -1$). For the cyanide ion, the self energy is given by (1). Madelung constants have been calculated by Bertaut's method,[13] in terms of a standard interionic separation R. This technique is well known and has been discussed in detail elsewhere [14] The Madelung energy (U_M) is the term $LA(R)e^2/(4\pi\varepsilon_0 R)$: by combining this term with equation (1), the electrostatic energy ($U_M - U_S$) may be written as in (2).

$$U_S = Lz_Cz_Ne^2/4\pi\varepsilon_0 r \qquad (1)$$

$$U_E = -\{[A(R)/R] + (z_Cz_N/r)\}(Le^2/4\pi\varepsilon_0) \qquad (2)$$

TABLE 1

Electrostatic energies

	$10^{10}R$/m	z_Cz_N	$A(R)$	$10^{-10}\{[A(R)/R] + (z_Cz_N/r)\}$m^{-1}	Summation limit/RU
(*a*) Na[CN]					
(i) NaCl type, 298 K	2.946 5	0	1.747 56	0.593 10	
(*ii*) Orthorhombic, point charge, 297 K, $r = 1.05 \times 10^{-10}$ m	2.82	0	1.658 67	0.588 18	4.8
(*iii*) Orthorhombic, distributed charge, 279 K, $z_N = -0.60$, $r = 1.05 \times 10^{-10}$ m	2.82	0.24	1.023 93	0.591 67	4.8
(*b*) K[CN]					
(*i*) NaCl type, 298 K	3 263 5	0	1.747 56	0.535 49	
(*ii*) Orthorhombic, point charge, 213 K, $r = 1.08 \times 10^{-10}$ m	3.02	0	1.621 24	0.536 83	4.6
(*iii*) Orthorhombic, distributed charge, 213 K, $z_N = -0.60$, $r = 1.08 \times 10^{-10}$ m	3.02	0.24	0.956 42	0.538 92	4.6

Thus, in the compounds studied, z_Cz_N/r acts as a modifier in the Madelung term. The results of this calculation are listed in Table 1. Structural data for the alkali-metal cyanides were taken from Wyckoff.[15] The orthorhombic structures of Na[CN] and K[CN] are symmetrical in energy for interchange of either site or charge of C and N. The rock-salt structure is found for Na[CN] and K[CN] at 298 K. The $[CN]^-$ ions have orientational disorder, with the CN axes lying mostly along ⟨100⟩ and ⟨111⟩,[16] consistent with *m3m* symmetry. The ions become locked in definite orientations in the orthorhombic polymorphs, with an approximately octahedral arrangement, at 279 (Na[CN] and 213 K (K[CN]).

Repulsion Energy.—A conventional repulsion potential, U_R, of the form $B\exp(-R/\rho)$ was adopted. As in previous work,[14] B was eliminated from equilibrium considerations and ρ was calculated from compressibility data. The compressibility of K[CN] in the rock-salt structure type has been measured by Haussühl; [17] for the other structures considered in this paper, compressibilities were obtained through molar-volume proportionalities.[14] Data related to the repulsion energy are listed in Table 2. In the absence of data on the temperature and pressure variation of compressibility, $\phi(T,P)$ in equation (5) was taken as unity.

An alternative model for the repulsion potential was proposed by Jenkins and Waddington.[18] While it is more detailed than that adopted here, there is no evidence that it is more satisfactory. In ionic structures, any repulsion potential which is equivalent to a high inverse power of the interionic distance will give results which are self consistent within experimental error. It is considered that the repulsion term used here is adequate for the following reasons. The repulsion energy is only *ca.* 10% of the electrostatic energy and, therefore, small errors in U_R have relatively less effect on the cohesive energy. The distances between atoms within a complex ion are, generally, much less than

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[13] F. Bertaut, *J. Phys. Radium*, 1958, **13**, 499.

[14] M. F. C. Ladd, *J.C.S. Dalton*, 1976, 1248.

[15] R. W. G. Wyckoff, ' Crystal Structures,' Wiley, New York, 1963, vol 1.

[16] J. M. Rowe, D. G. Hinks, D. L. Price, and S. Susman, *J. Chem. Phys.*, 1973, **58**, 2039.

[17] S. Haussühl, *Naturwiss.*, 1957, **44**, 525.

[18] H. D. B. Jenkins and T. C. Waddington, *Chem. Phys. Letters*, 1975, **31**, 369.

those between ions. The species of the complex ion represents a space-filled structural unit, and the compression of the solid will take place mainly with respect to interionic space. Notwithstanding that the energy minimisation has been carried out without inclusion of the multipole effects,[18] the results are satisfactory. It is to be expected that the repulsion potentials in the cubic point-charge models ($d = 0$, ref. 18) and in the orthorhombic distributed-charge models of these cyanides will be similar, particularly near to the transition temperature: the pairs of ρ/R values (Table 2) achieve this condition. Furthermore, as Table 4 shows, the agreement in $U(R)$ between the point-charge and distributed charge models is rewarding.

TABLE 2

Repulsion-energy data

	$10^{11}\kappa$/ N^{-1} m^2	$10^4\beta$/ K^{-1}	$\phi(T,P)$	$[10^{19}(3vT\beta/\kappa)]$/ J	$10^{10}\rho$/ m	ρ/R
Na[CN] (i)	5.14	1.2	1	1.068	0.337	0.114
K[CN] (i)	6.95	1.1	1	0.979	0.359	0.110
Na[CN] (iii)	5.04	1.2	1	1.000	0.324	0.115
K[CN] (iii)	6.74	1.1	1	0.700	0.341	0.113

TABLE 3

Dispersion-energy data

	Na[CN] (i)	K[CN] (i)	Na[CN] (iii)	K[CN] (iii)
$10^{10}R$/m	2.946 5	3.263 5	2.82	3.02
10^{10} Summation limit/m			193	207
S_{+-}	6.595 2	6.595 2	5.145 1	4.413 6
$S_{++} = S_{--}$	1.806 7	1.806 7	1.495 9	1.249 2
T_{+-}	6.145 7	6.145 7	4.425 8	3.626 1
$T_{++} = T_{--}$	0.800 1	0.800 1	0.641 0	0.499 8
$10^{40}\alpha_+$/F m^2	0.95	2.7	0.95	2.7
$10^{40}\alpha_-$/F m^2	8.7	8.7	8.7	8.7
$10^{19}\varepsilon_+$/J	75.8	51.1	75.8	51.1
$10^{19}\varepsilon_-$/J	3.8	3.8	3.8	3.8
$10^{99}c_{+-}$/J F^2 m^4	44.9	125	44.9	125
$10^{99}c_{++}$/J F^2 m^4	51.3	280	51.3	280
$10^{99}c_{--}$/J F^2 m^2	216	216	216	216
p_+	11.8	13.4	11.8	13.4
p_-	2.0	2.0	2.0	2.0
$10^{119}d_{+-}$/J F^2 m^6	89.0	293	89.0	293
$10^{119}d_{++}$/J F^2 m^6	54.9	505	54.9	505
$10^{119}d_{--}$/J F^2 m^6	625	625	625	625
$10^{79}C$/J m^6	434	1 027	348	695
$10^{99}D$/J m^8	661	1 821	493	1 087

TABLE 4

Cohesive-energy and thermodynamic data

	Na[CN] (i)	K[CN] (i)	Na[CN] (iii)	K[CN] (iii)
(*a*) Electrostatic model				
$-U(R)$/kJ mol^{-1}	750	687	748	688
(*b*) Thermodynamic model [20] (298 K). All units are kJ mol^{-1}				
ΔH_f(MCN,s)	−89.8	−112.5		
ΔH_{sub}(M,s)	108.7	90.0		
I(M,g)	495.8	418.8		
$U(R) - nRT$	−755	−692		
ΔH_f(CN$^-$,g)	60.7 *	70.7 *		
ΔH_f(CN,g) [21]	445			
E(CN,g)	−379			

* Derived data.

Dispersion Energy.—The dispersion energy, U_D, included interionic dipole–dipole and dipole–quadrupole terms, terms in higher inverse powers of R being insignificant in the present context. The form of the dispersion energy has been discussed previously,[3,14] and a similar analysis was followed here. The dielectric constant of K[CN] has been measured by Haussühl.[17] It was used in the Clausius–Mossotti equation to calculate the polarisability of K[CN]. Using the value of $\alpha(K^+)$,[19] $\alpha(CN^-)$ was found to be 8.7×10^{-40} F m^2. In the interpretation of U_D, the cyanide ion was again regarded as a single entity. The lattice sums for the rock-salt structure type are well known. Those for the orthorhombic polymorphs were evaluated by direct summation of equations (8) and (11). The dispersion-energy data are listed in Table 3.

Cohesive Energy.—The cohesive energy was calculated from equations (3)—(12). The results are listed in Table 4, together with the thermodynamic data [20] relevant to the cycle for ΔU in Figure 1.

$$U(R) = -\Big(\{[A'(R)e^2][1 - (\rho/R)]/4\pi\varepsilon_0\} + \{C[1 - (6\rho/R)]/R^6\} + \{D[1 - (8\rho/R)]/R^8\} + (3vT\beta/\kappa)(\rho/R)\Big)L/10^3 \quad (3)$$

$$A'(R) = [A(R)/R] + (z_C z_N/r) \quad (4)$$

$$R/\rho = \{[9v\phi(T,P)/\kappa] + 2A'(R)e^2 + (42C/R^6) + (72D/R^8)\}/\{[A'(R)e^2] + (6C/R^6) + (8D/R^8) - (3vT\beta/\kappa)\} \quad (5)$$

$$\phi(T,P) = 1 + \{T[(\partial\kappa/\partial T)_P/\kappa] + \beta(\partial\kappa/\partial P)_T + (2\beta/3)\} \quad (6)$$

$$C = [S_{ij}c_{ij} + (S_{ii}c_{ii}/2) + (S_{jj}c_{jj}/2)]/16\pi^2\varepsilon_0^2 \quad (7)$$

$$c_{ij} = (3/2)\alpha_i\alpha_j\varepsilon_i\varepsilon_j/(\varepsilon_i + \varepsilon_j) \quad (8)$$

$$S_{ij} = R^6 \sum_{ij} (1/R_{ij}^6) \quad (R_{ij} \neq 0) \quad (9)$$

$$D = [T_{ij}d_{ij} + (T_{ii}d_{ii}/2) + (T_{jj}d_{jj}/2)]/16\pi^2\varepsilon_0^2 \quad (10)$$

$$d_{ij} = (9/4)(c_{ij}/e^2)[(\alpha_i\varepsilon_i/p_i) + (\alpha_j\varepsilon_j/p_j)] \quad (11)$$

$$T_{ij} = R^8 \sum_{ij} (1/R_{ij}^8) \quad (R_{ij} \neq 0) \quad (12)$$

$$p_i = [(4\pi^2 m\varepsilon_i\alpha_i/h^2e^2)n_i]^{\frac{1}{2}} \quad (13)$$

DISCUSSION

The *ab initio* calculations of atomic charges on [CN]$^-$ give results which seem more reasonable than those from the CNDO/2 and INDO methods. The cohesive energy itself is not a good discriminator of the details of its calculation. For example, the INDO values of z_C and z_N give, as a product, sensibly the same value for U_S as do the results from the *ab initio* calculation, although the latter results are, individually, the more acceptable for atomic charges. Although the inclusion of the self-energy term is required in the distributed-charge model, the effect on U_E is not significantly different from that for the point-charge model. If, in the orthorhombic forms of Na[CN] and K[CN], z_N is varied by 0.05, the change in $U(R)$ is only *ca.* 1 kJ mol^{-1}. Further refinement of the distributed-charge model requires a corresponding precision in the other structural and physical parameters of the calculation.

The symmetry of the orthorhombic structures does not permit distinction between the C and N sites in the crystal, with respect to cohesive energy. Such a distinction should be possible, however, by modern *X*-ray analysis. Lithium cyanide does not show this same

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[19] M. F. C. Ladd, *J. Chem. Phys.*, 1974, **60**, 1954.

[20] Nat. Bureau Stand., Circular no. 500, 1952; Technical Note 270-3, 1968.

symmetry, but it was not felt sufficiently useful to repeat the earlier calculation [3] on this compound. From thermodynamic data,[20] included in Table 4, the heat of formation of the gaseous $[CN]^-$ ion at 298 K is 66 ± 5 kJ mol^{-1}. The precision of this result may be increased by including results from other alkali-metal cyanides, but the magnitude is unlikely to be sensibly affected. Taking [21] $\Delta H_f(CN,g)$ as **445** kJ mol^{-1}, the electron affinity of the gaseous CN species is -379 kJ mol^{-1}, in good agreement with the experimental value [21] of -369 kJ mol^{-1}. The m.o. results for the energy change of the process $CN(g) \longrightarrow [CN]^-(g)$ were unsatisfactory and, at this stage, cannot be said to supplant the thermodynamic value.

APPENDIX

$A(R)$	Madelung constant referred to the distance R
$A'(R)$	Madelung term modified by the electrostatic self energy
B	Constant of the repulsion potential
C	Constant of the dipole–dipole van der Waals potential
D	Constant of the dipole–quadrupole van der Waals potential
c_{ij}	London dispersion dipole–dipole parameter for the ij ion pair
d_{ij}	Dispersion dipole-quadrupole parameter for the ij ion pair
e	Electronic charge $= 1.602\,1 \times 10^{-19}$ C
h	Planck constant $= 6.625\,6 \times 10^{-34}$ J s
m	Mass of the electron $= 9.109\,1 \times 10^{-31}$ kg
n_i	Number of electrons in the outer shell of the ith ion
p_i	Electron number in the dipole–quadrupole parameter for the ith ion
RU	Reciprocal-space unit
R	Distance basis for the cohesive-energy calculations
r	Shortest (C–N) interatomic distance in a structure
R_{ij}	Distance between the ith and jth ions in a structure
S_{ij}	Structural constant of the dipole–dipole potential
T_{ij}	Structural constant of the dipole–quadrupole potential
U_D	Dispersion energy
U_E	Electrostatic energy
U_M	Madelung energy
U_R	Repulsion energy
U_S	Self energy
$U(R)$	Cohesive energy referred to a basis distance R
$\langle UVW \rangle$	Crystallographically equivalent directions in a structure
v	Volume per ion pair
z_i	Charge on the ith species
α_i	Polarisability of the ith ion
β	Volume expansivity
ε_i	Characteristic energy of the ith ion
ε_0	Permittivity of a vacuum $= 8.854\,185 \times 10^{-12}$ F m^{-1}
κ	Compressibility (isothermal)
$\phi(T,P)$	Hildebrand equation of state correction
ρ	Exponent in the repulsion potential
$(\partial\kappa/\partial P)_T$	Pressure coefficient of compressibility
$(\partial\kappa/\partial T)_P$	Temperature coefficient of compressibility
$E(X,g)$	Electron affinity of the gaseous X species
$\Delta H_f(X,y)$	Enthalpy of formation of the X species in state y
$\Delta H_{sub}(X,s)$	Enthalpy of sublimation of the solid X species
$I(X,g)$	Ionization energy of the gaseous X species
n	Number of species per formula weight
P	Pressure
R_0	Gas constant $= 8.314\,3$ J K^{-1} mol^{-1}
T	Temperature
ΔU	Thermodynamic cohesive energy, comparable to $U(R)$

Note added in proof: further evidence for $z_N \approx 0.60$ in the $[CN]^-$ ion has been reported in a recent publication (H. D. B. Jenkins and K. F. Pratt, *J. Inorg. Chem.*, 1976, **38**, 1775).

[6/387 *Received, 25th February,* 1976]

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[21] J. Berkowitz, W. A. Chupka, and T. A. Walter, *J. Chem. Phys.*, 1969, **50**, 1497.