The Shapes and Energetics of Dimeric Lithium and Sodium Cyanides. *Ab Initio* Molecular-orbital Calculations †

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The geometries and energies of many different isomers of $(LiCN)_2$ and $(NaCN)_2$ have been investigated by *ab initio* molecular-orbital calculations, employing large gaussian basis sets with both polarization and diffuse functions. The geometries were fully optimized by gradient techniques. For both dimers, there are three different isomers of very similar stability. The energy difference between the lowest-energy structure, a four-membered planar ring of alternating M (M = Li or Na) and N atoms of D_{2h} symmetry, and two different six-membered planar rings of C_{2h} and C_{2v} symmetries, is *ca.* 20 kJ mol^{-1} for $(LiCN)_2$ but only 5 kJ mol^{-1} for $(NaCN)_2$. Linear structures are substantially less stable. No non-planar isomers were found to be local energy minima.

It has recently been shown, by microwave spectroscopy, that monomeric sodium [1] and potassium [2] cyanides are neither linear cyanides, MCN, nor linear isocyanides, MNC. Instead, they are ' T-shaped ', or perhaps ' L-shaped ' species, in which the metal ion approaches the cyanide group ' sideways,' and is roughly equidistant from C and N, with M–N–C angles of 81.4° in NaCN [1] and 85.7° in KCN.[2,3] One may well doubt whether many chemists could successfully have predicted these shapes, given the traditional linear cyanide structure adopted by HCN, which is *ca.* 43 kJ mol^{-1} lower in energy than HNC,[4] or the linear isocyanide arrangement reported for ' LiCN ' from vibrational analyses of the isotopic shifts of the matrix-isolated species,[5,6] and very recently confirmed by molecular-beam electric resonance techniques.[7]

These unexpected results for KCN prompted several *ab initio* molecular-orbital studies.[8-10] The main features of the experimental shape of KCN were satisfactorily reproduced, although unusually flexible basis sets for C and N were required.[9,10] *Ab initio* predictions [9,10] of the structure of NaCN were published before the experimental results were available, and thus cannot be accused of bias. All three independent geometrical parameters for NaCN were predicted to within one experimental standard deviation by those calculations which included the correlation energy and its influence on geometry.[10]

Alkali-metal cyanides are highly polar species, with bonding of a mainly electrostatic nature. Electronic factors therefore favour dimers, trimers, and higher polymers over monomers, and the proportion of monomers in the vapour will be low, except at exceedingly high temperatures and low pressures. Structural characterization of the dominant oligomers does not at present seem to be experimentally feasible. Microwave spectroscopy will be of limited use, since the oligomers are either non-polar or of very low polarity compared to the monomers, even before considering the difficulties associated with isotopic substitution. Electron diffraction is restricted by the apparent impossibility of generating the relatively high pressure for a homogeneous beam which this technique requires.

In principle, vibrational spectroscopy of matrix-isolated species can provide sufficient information to determine point-group symmetries of polar oligomers. In practice, however, very complex spectra have been obtained for alkali-metal cyanides.[11,12] It was found difficult to distinguish, with any certainty, dimer bands from those of higher oligomers, and the possibility of more than one dimeric isomer seemed likely for $(LiCN)_2$.[11] One severe problem with the application of spectroscopic techniques to these polar oligomers is that there is insufficient experience, at present, of the vibrational properties of such systems to permit a non-arbitrary assignment of several of the fundamental modes. The determination of symmetries is therefore of uncertain reliability.

It has already been shown that *ab initio* calculations can give a satisfactory account of the shapes and structures of alkali-metal cyanide monomers.[8-10,13,14] I now extend this work to include lithium and sodium cyanide dimers.

Calculational Procedures

All calculations made use of the program GAUSSIAN 80,[15] implemented on a VAX 11/780. Geometries were optimized by gradient techniques,[16] subject to the symmetry constraints indicated in Figures 1 and 2. Parameters reported here converged to better than 0.1 pm or 0.1°. The split-valence 4-31G [17] basis set was used for geometry optimization. A single calculation, with the larger, polarized, 6-31G* [18] basis was performed for each structure at the converged geometry. However, *d* functions were not included for Li or Na, as their use produces insignificant changes for the monomers.[10,19] As no 4-31G or 6-31G bases have been published for sodium, I used 9*s*5*p* and 11*s*7*p* sets,[20] contracted to 5*s*3*p* and 6*s*4*p*.

At this juncture, three different structures were found to be very close in energy for both $(LiCN)_2$ and $(NaCN)_2$. For a final calculation for each of these, structures (I)—(III) in Figures 1 and 2, the 6-31G* basis was augmented with diffuse *p* functions on both C and N. It has been shown that these are necessary for an accurate description of the relative energies of systems containing atoms bearing a substantial negative charge.[21] This additional refinement was not felt to be necessary for structures (IV)—(VIII), which were substantially higher in energy than (I)—(III).

Results

The main body of results for $(LiCN)_2$ and $(NaCN)_2$ is presented in Figures 1 and 2. Optimized geometrical parameters (bond lengths in pm, angles in degrees), together with point-group symmetries for the non-linear cases, are given for each of the eight different structures found to be a local energy minimum for $(LiCN)_2$ and $(NaCN)_2$. Structures for MCN and MNC, optimized at the same computational level, are also reported. Absolute energies for the monomeric isocyanides and for the most stable dimeric forms are given, as are relative energies, in kJ mol^{-1}, for the monomeric cyanides and for the remaining dimeric structures. Energies for the cyanide monomers are relative to the isocyanides, and for the dimers are relative to the most stable dimeric isomer, structure (I).

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† *Non-S.I. units employed*: D ≈ 3.34×10^{-30} C m; a.u. = 2 625.5 kJ mol^{-1}.

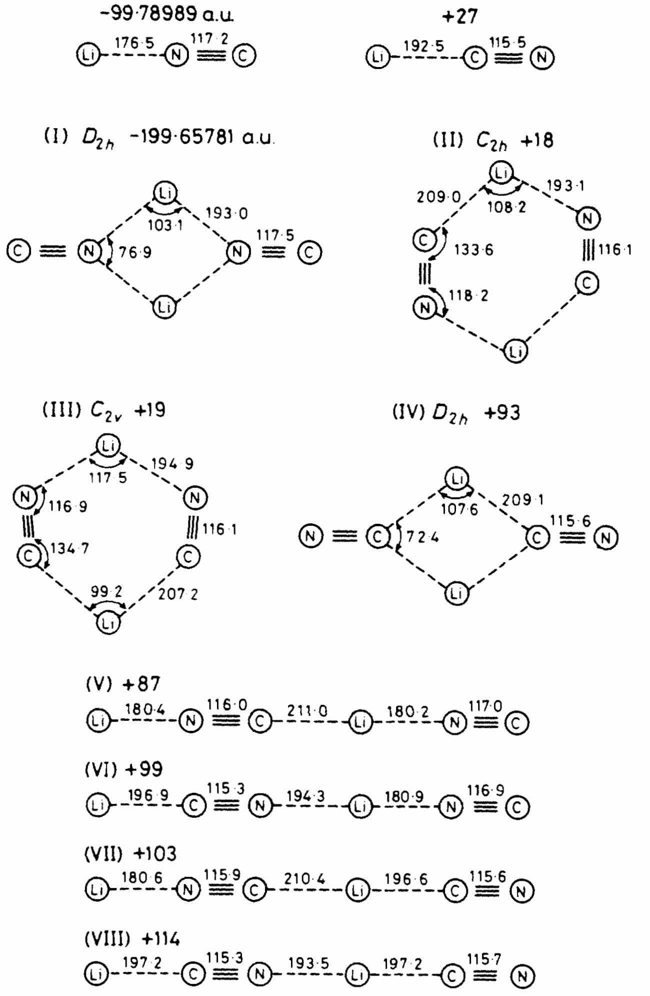

Figure 1. Optimized geometries and energies for different LiCN and $(LiCN)_2$ isomers. Bond lengths in pm, angles in degrees. Energies for LiNC and isomer (I) of $(LiCN)_2$ are in atomic units, for LiCN in kJ mol^{-1} relative to LiNC, and for isomers (II)—(VIII) in kJ mol^{-1} relative to (I). Point-group symmetries of non-linear isomers are given

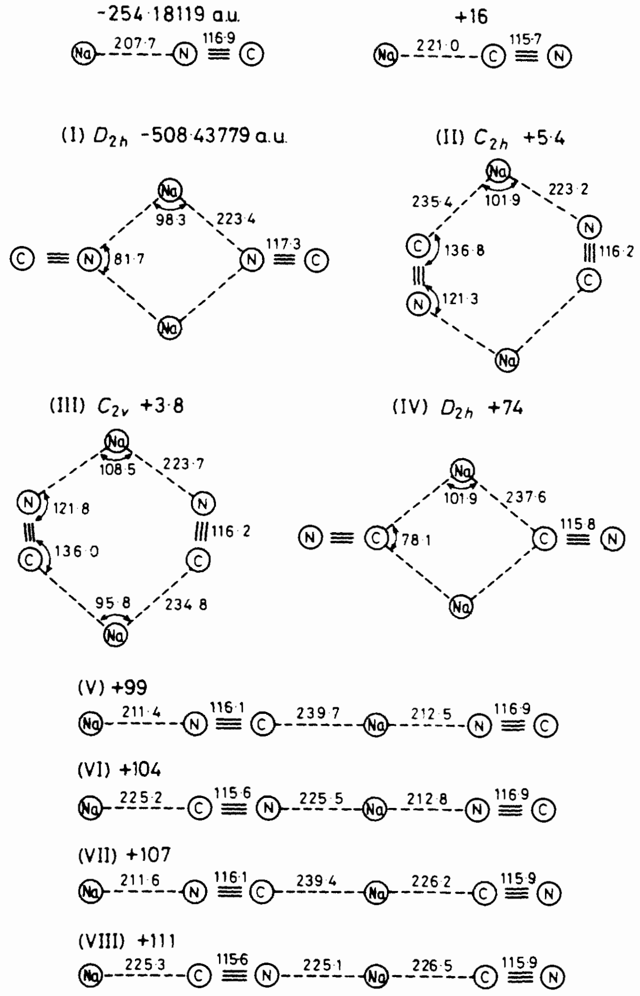

Figure 2. Optimized geometries and energies for different NaCN and $(NaCN)_2$ isomers. Bond lengths in pm, angles in degrees. Energies for NaNC and isomer (I) of $(NaCN)_2$ are in atomic units, for NaCN in kJ mol^{-1} relative to NaNC, and for isomers (II)—(VIII) in kJ mol^{-1} relative to (I). Point-group symmetries of non-linear isomers are given

Energies for the monomers and dimers (I)—(III) result from the basis 6-31G* augmented with diffuse *p* functions. Energies for structures (IV)—(VIII) result from the 6-31G* basis without diffuse *p* functions, and are relative to the energy of structure (I) obtained at the same level.

It is clear that the shapes and relative energies of the various dimeric forms of $(LiCN)_2$ and $(NaCN)_2$ are similar, even though the monomers have quite different equilibrium structures.[1,5-7,9,10,13,14] It is also apparent that the energy differences between several different dimeric arrangements are very small, and thus the degree of reliability to be expected from the present calculations is as important as the results themselves. There are several aspects to address, among them the geometries obtained, the deficiences in the basis sets used, and the complete neglect of correlation energies.

I consider first the optimization of geometries using a relatively modest split-valence basis set. Improvements to this, such as the inclusion of polarization functions, would be expected to shorten bonds slightly, by *ca.* 1—2%, but this trend would be reversed by inclusion of the correlation energy, which usually modestly increases bond distances. I suggest therefore that it is unlikely that significant errors have been introduced by the procedures adopted. To support this contention, I note that the optimized bond lengths in LiNC, Li–N 176.5 pm and N–C 117.2 pm, compare most favourably with the experimental values[7] of 176.0(6) pm and 116.8(6) pm, respectively.

The basis used to calculate final energies contained polarization functions and, for the most important structures, diffuse *p* functions on C and N as well. It therefore seems unlikely that the relative energies of structures (I)—(III) would be changed by more than about 10 kJ mol^{-1}, at the Hartree–Fock limit. Diffuse functions favour structure (I) slightly, but polarization functions modestly favour (II) and (III), so further improvements of both types would cause only very minor relative changes.

Post-SCF studies have shown that the L-shaped and linear cyanide monomer isomers have similar correlation energies, which differ by scarcely 1 kJ mol^{-1},[10,18] and that both are greater than that of the isocyanide by about 12—15 kJ mol^{-1},[10,19,22] for both lithium and sodium systems. It thus appears likely that inclusion of the correlation energy would favour structure (II) or (III) at the expense of (I), but it is not possible to be dogmatic on this point, and the appropriate calculations are not feasible for me. I adopt, tentatively, a possible uncertainty of 15 kJ mol^{-1} for the relative energies of structures (II) or (III) compared to (I), due to neglect of correlation energy.

Thus the combination of these aspects leads to an estimated worst-case uncertainty of 25 kJ mol^{-1} for the relative energies of the structures (I)—(III) for both $(LiCN)_2$ and $(NaCN)_2$. Since the calculated energy differences are smaller than this upper limit, the present calculations unfortunately cannot establish with certainty which geometrical arrangement has the lowest energy, especially for $(NaCN)_2$ for which there are three possible isomers within 6 kJ mol^{-1}. I feel confident, however, that none of the structures (IV)—(VIII) could be the minimum-energy form.

Several different geometrical arrangements for $(MCN)_2$ were studied in addition to those displayed in Figures 1 and 2. Since monomeric NaCN favours a structure in which Na^+ is bound ' sideways ' on to CN^-,[1,9,10] related geometries were investigated for $(MCN)_2$. A planar, four-membered ring was built up from the two M^+ ions and two points along the C≡N directions, with the C≡N axes perpendicular to the plane of the four-membered ring, and either parallel or antiparallel to each other. However, structures of this type are not local minima, but were found to relax towards (I), (II), or (III) depending upon the point of departure. In a similar fashion, linear structures containing the two M^+ ions and two points along the C≡N axes perpendicular to the chain direction were also found not to be local minima. The four-membered ring isomers (I) and (IV) were perturbed by puckering, but found to be most stable when planar, as expected for primarily electrostatic binding.

Discussion

Many of the themes displayed in Figures 1 and 2 have already been expounded and partially developed in studies of MH and MF dimers.[21,23–25] Perhaps the most important general observation is that cyclic structures are more stable than linear isomers. This is scarcely unexpected, since purely electrostatic interactions are more favourable for cyclic than linear arrangements, and the binding within MCN dimers is predominantly electrostatic in nature, as discussed below. Cyanide dimers differ from $(MH)_2$ and $(MF)_2$ in their greater structural richness and diversity. My calculations have shown that there are three different isomers of both $(LiCN)_2$ and $(NaCN)_2$ which are so close in energy that the present work is unable to determine with certainty which is the most stable. It is likely that all three forms are present in significant amounts in the vapour; this point is considered in more detail later.

The potential surfaces for LiCN and NaCN monomers [10,13,14] show little energy change as the M^+ ion is moved with respect to the CN^- unit. This ' polytopic ' bonding [13] may be rationalized as a consequence of the almost uniform charge distribution within the CN^- ion; net atomic charges [26] on both C and N are close to -0.5 e for basis sets of the quality used here, although precise values are sensitive to minor details of the basis. Given the relatively flat potential-energy surfaces for the monomers, the existence of several local minima for the dimers, with their substantially greater number of geometrical degrees of freedom, is unremarkable. Nor is it surprising that the four-membered ring isomer (I), with M $\cdots$ N contacts, is more stable than (IV), which is more cyanide-like, since for both lithium and sodium monomers the isocyanide isomer is more stable than the cyanide. What *is* surprising is the magnitude of the energy difference between (I) and (IV), *ca.* 40 kJ mol^{-1} greater than twice the difference between MNC and MCN, and I see no simple rationalization for this.

Sodium cyanide monomer adopts an ' L-shaped ' structure, in which sodium is almost equidistant from both carbon and nitrogen.[1,9,10] This architecture is most closely simulated by isomers (II) and (III), whose relatively low energy, especially for sodium, is thus to be expected. However, it is puzzling that three-dimensional dimer analogues of the L-shaped monomer structure are found not to be local energy minima, as outlined at the end of the Results section. The relative energies of the linear dimers follows from that of the linear monomers. In $M_aX_aY_aM_bX_bY_b$ (X, Y = C or N), the interaction between Y_a and M_b is relatively weak, as judged by the internuclear distance, which is substantially greater than in MYX monomer, while the other distances are only marginally changed by dimer formation. Thus MNCMNC, for example, can be regarded as two slightly perturbed MNC units, linked together fairly weakly; since MNC is more stable than MCN, MNCMNC is the most stable linear dimer and MCNMCN the least. As the energy difference between MNC and MCN is greater for Li than Na, it follows that the difference between structures (V) and (VIII) will also be greater for Li than Na.

For the four-membered ring isomers (I) and (IV), I note that the angles at M are substantially wider than those at C or N. It has been argued [24,25] that cross-ring covalent bonding interactions between the M species are responsible for this angular pattern. Others [21] have preferred to argue in terms of effective size or ionic radius. Since cations typically have smaller radii than do anions, one expects closer M $\cdots$ M than N $\cdots$ N or C $\cdots$ C contacts, with consequently larger angles at M. Several aspects of the present work support this approach. In my calculations, the Li $\cdots$ Li or Na $\cdots$ Na overlap populations [26] in structures (I) and (IV) are always *negative*, from which one may infer their interaction to be repulsive. The Li $\cdots$ Li distances in (I) and (IV) differ only slightly, as do the Na $\cdots$ Na distances, consistent with the idea that steric interactions are important. However, there are other aspects of the structures presented in Figures 1 and 2 which imply that steric considerations are not of overwhelming importance. For example, the N $\cdots$ N distance in $(NaCN)_2$, structure (I), exceeds that in $(LiCN)_2$, structure (I), by about 10%, and similar behaviour is found for the C $\cdots$ C distances in isomers (IV). The angles in isomers (II) and (III), while consistent with each other, are difficult to rationalize on a steric viewpoint, as the C $\cdots$ C distance in (III) is *less* than the N $\cdots$ N distance, by about half the margin by which the C $\cdots$ C distance in (IV) exceeds the N $\cdots$ N distance in (I).

Isomer (III) is the only polar dimer structure of low enough energy to be present in significant amounts in the vapour. Its dipole moment is calculated to be 1.5 D for $(LiCN)_2$ and 1.0 D for $(NaCN)_2$, values much lower than predicted for the monomers (LiNC, 9.0 D; ' L-shaped ' NaCN, 9.2 D). Experimental values for the monomers are not available, but as basis sets of the size used here give very satisfactory dipole moments for highly polar species such as LiF, the calculated values for MCN and $(MCN)_2$ are probably fairly reliable. Since the intensities of microwave transitions depend on the square of the dipole moment, the probability of microwave detection of the dimers appears remote at present, especially in view of the more favourable energy-level distribution for the monomers.

The i.r. spectra of LiCN and NaCN vapours trapped in inert matrices have been studied, and several peaks assigned to dimers.[11,12] A structure of type (IV) was assumed for $(NaCN)_2$, but type (I) for $(LiCN)_2$. While a type (IV) structure can definitely be excluded by the present *ab initio* calculations, the difference in spectra between the two structures would be slight. Additional bands were seen for $(LiCN)_2$[11] which could not plausibly be assigned to an isomer of type (I). In particular, there were too many 'Li–N' or 'Li–C' stretching vibrations in the 500—700 cm^{-1} region. In the light of the *ab initio* results presented here, these difficulties not only disappear, but indeed could have been anticipated. Isomers (II) and (III) will certainly have a multiplicity of peaks in that region, and the implication of the matrix-isolation work is that they are present in significant amounts in the vapour, consistent with the modest energy separation found here between (I) and (II) or (III).

Dimerization energies at absolute zero, uncorrected for zero-point vibrational energies, are found here to be −205 kJ per mol of dimer for LiCN, and −198 kJ mol^{-1} for NaCN. The reduced magnitude for NaCN is a direct consequence of the greater distances involved, which produce reduced electrostatic binding energies in both monomer and dimer, with a smaller difference between them. There is an experimental value for the dimerization enthalpy of NaCN,[27] of 172 ± 13 kJ mol^{-1} at 1 000 K. However, this quantity was derived indirectly, and relies on several assumptions some of which are now known to be incorrect. A direct comparison with the present *ab initio* values involves vibrational and rotational entropy and internal energy contributions, which cannot all be calculated precisely. The best estimates are that $\Delta E^0_{1\,000} = -152 \pm 20$ kJ mol^{-1} from experiment, and -167 ± 15 kJ mol^{-1} *ab initio*; however an appreciable part of the uncertainty in both values arises from the same source, the lowest-frequency vibrational modes in $(NaCN)_2$. A correction for the basis-set superposition error would reduce the magnitude of the *ab initio* result by perhaps as much as 10 kJ mol^{-1}, and bring the two values into very satisfactory agreement.

An interesting area of concern involves the degree of covalent binding in MCN and $(MCN)_2$, whether it is greater than in MF or $(MF)_2$ systems, and whether LiCN differs substantially from NaCN. Perhaps the most straightforward way to address this point is to inspect the population analyses,[26] which show essentially complete electron transfer from Na to CN, but only *ca.* 60% for Li to CN. However, since population analyses are notoriously sensitive to minor details of basis sets, this comparison should be regarded as no more than semi-quantitative. The C≡N distances in MNC and MCN differ slightly, which presumably would not occur for wholly electrostatic binding. As the difference is substantially greater for M = Li than Na, this supports the notion of greater covalent character in the lithium system, as does the greater energy difference between lithium isocyanide and cyanide. Some further evidence for covalent interactions may be provided by the variation in M···N or M···C distances, which are typically 8—10% greater when N or C is co-ordinated to two M species, as in structure (I) or (IV), or when one M is co-ordinated to two N or C, as in (II) or (III), than in the monomers. However, similar variations are found when comparing $(MF)_2$ with MF,[21,23] so there is little reason to suppose that the ionic character of MCN differs greatly from that of MF.

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