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Two hypothetical structures of solid FCN

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Summary. A Hartree–Fock-based Self-Consistent Crystal Field (HF-SCCF) method is applied to the structure and lattice energy of solid FCN. This structure has not been experimentally determined and hence the present study is the first attempt to do so, either by theory or by experiment. The crystal space groups considered are the polar HCN analog and the non-polar ClCN analog. Both crystal structures were varied to minimize the lattice energy and 4.8 kcal/mol and 3.9 kcal/mol were obtained for the polar and non-polar arrangements, respectively. Comparisons to the other cyanogen halide solids, $HCN_{(S)}$ and $HF_{(S)}$ are made.

Key words: FCN – HF-SCCF – Lattice energy

1 Introduction

The understanding of the intermolecular interactions in molecular crystals in terms of Pauli repulsion, van der Waals attraction and the Coulomb interaction with the infinite lattice, is a corner stone in the conceptual framework of solid state chemistry. Hence, the successes and failures of this assumed separability in specific cases are of great importance.

In the present study, the first estimates of the lattice energy and structure of solid cyanogen fluoride will be presented. Cyanogen fluoride is hard to handle in large quantities, since it is highly volatile and poisonous. In spite of this, large quantities were produced by Fawsett and Lipscomb [1]. The melting and boiling points were determined to − 82°C and − 46°C respectively. Hence, while both the liquid and the gas [2] phases are characterized, the description of the solid is incomplete, since the crystal structure is unknown. The fact that this information is missing makes $FCN_{(S)}$ unique among the stable cyanogen halides.

The solids of ClCN [3], BrCN [4] and ICN [5] are all found to constitute from arrangements of axial chains. Solid ICN differs from the other two in that the chains are arranged in a trigonal polar structure, as compared to the orthorombic non-polar arrangements of the two former solids. The present study addresses two hypothetical structures of solid FCN being the orthorombic polar HCN analog and the non-polar ClCN and BrCN analog.

The computational approach assumed is the Hartree–Fock based Self-Consistent Crystal Field (HF-SCCF) method, which consistently employs the above separation of energy contributions to efficiently compute the lattice energy of a molecular crystal. The method is described in [6–8] and applied to the lattice energy, structures and properties of solid hydrogen cyanide [6,7,9] and to the lattice energy and structure of solid hydrogen fluoride [10]. Hence, in [6] the HF-SCCF procedure was outlined and an efficient Ewald summation technique described. In [7] the intermolecular Pauli repulsion and dispersion interaction were introduced. The Pauli repulsion expression enters as an iterative first order renormalization correction to the Coulombic interaction and being *ad hoc*, a parameter can be introduced and fitted to an experimental observable or to *ab initio* calculations on the dimer. The dispersion interaction expression in [7] is particularly attractive since it couples general multipole polarizabilities in contrast to the conventional coupling of dipole polarizabilities. This description of the intermolecular interactions was sufficient to unambiguously discard the proposed non-polar structure of solid HCN [11] in favour of the polar structure suggested originally by Dulmage and Lipscomb [12]. The lattice energetics obtained in [7] is in excellent agreement with estimates obtained by Rae [13]. The components of the dielectric constant tensor and shifts in dipole moment gradients, in going from the gas phase to the solid, are computed in [9] in qualitative agreement with experiment. Furthermore, the free-solid shifts in intramolecular distances are predicted in [9], since this effect is still not experimentally determined. In [8] the intermolecular interactions in the FCN dimer, as obtained from *ab initio* calculations, were quantitatively resolved in terms of the above conceptual approach. The *ad hoc* Pauli repulsion expression was found to be sufficient to reproduce the results at the Hartree–Fock level of theory, while a similar renormalization correction expression was introduced at the MP2 level to perfect the fit at that level of theory.

A main purpose of the study on the FCN dimer [8] was to produce *ab initio* parameters for the renormalization corrections, to be used in the present study, since no experimental information on the structure of the solid is available.

An alternative to the HF-SCCF approach is to perform an *ab initio* Hartree–Fock calculation on the infinite crystal (see e.g. [14–16] and references therein). That approach is bound to fail in cases where dispersion interaction is vital. It corresponds to 55% of the total lattice energy in $HCN_{(S)}$ [7] while the nitrogen and acetylene [17] solids fall apart at the Hartree–Fock level of theory. A second short-coming of *ab initio* Hartree–Fock is the inherent superposition error, which is of the same order of magnitude as the total lattice energy for the above mentioned systems and basis sets chosen.

2 Computational details

2.1 The molecular description

In the present study, the same intramolecular description as in [8], including bond distances and a $6\text{-}31G^{++}$ basis set, has been employed. Detailed analyses of basis set effects and coupling between intra- and intermolecular degrees of freedom are premature at this stage, since a description of intramolecular electronic near degeneracies is missing. Support for decoupling of intra- and inter-molecular degrees of freedom are obtained from the study on solid HCN [9], where this effect was found to be negligible.

2.2 *On the choice of hypothetical structures*

The critical structural hypothesis of the present study is that the crystal structure of $FCN_{(S)}$ is either a polar $HCN_{(S)}$ analog or a non-polar solid $ClCN_{(S)}$ analog, both structures consisting from axial arrangements of chains. The main arguments in favour of this hypothesis are the obvious similarities in molecular structures and all three molecules having sizable dipole moments [2].

2.3 *On the renormalization parameters*

It should be noted here that the value of the Pauli repulsion parameter, obtained for the FCN dimer [8] ($k_1 = 0.68$), agrees excellently with that obtained for the non-polar structural candidate of HCN ($k_1 = 0.66$) [7]. This serves as a consistency test for the intuitive similarity between the two systems. Furthermore, it was noted in [7] that in the case of the polar structural candidate, a Pauli repulsion parameter $k_1 = 0.96$ was needed to reproduce the experimentally observed intermolecular distance along the hydrogen-bonded chains. It was implied in [7] that this is due to the lattice field tendency to compress the unit cell, in conjunction with too soft a Pauli repulsion functional description for small intermolecular separations.

The similar parametrizations of the Pauli repulsion for the *non-polar* FCN dimer and $HCN_{(S)}$, suggest that the analogy can be brought one step further in that the Pauli repulsion parameter for the *polar* $FCN_{(S)}$ structural candidate is taken equal to that for the corresponding $HCN_{(S)}$ structure.

3 Results and discussion

3.1 *The non-polar ClCN structural analog*

The renormalization parameters obtained from the study on the dimer, were assumed. Both tetragonal and orthorombic structures were considered. These arrangements are depicted in Fig. 1a. For the tetragonal *P4/nmm* structure a unit cell with dimensions $a = b = 9.0$ bohr and $c = 10.2$ bohr is obtained. The energy contributions for the optimization of a are shown in Fig. 2a. In Fig. 2b the system is shown to have an orthorombic *Pmmn* optimal structure with $a = 8.5$ bohr and $b = 9.2$ bohr and a lattice energy of 3.9 kcal/mol. The non-polar structure contains one additional degree of freedom, $R\|$ (see [7, 8] for definition), corresponding to a transverse relative displacement of the antiparallel chains. The truly minor energy dependence in this degree of freedom is shown in Fig. 2c for the tetragonal structure. The data for the FCN *Pmmn* structure are displayed in Table 1, where they are compared to the experimentally obtained values for $ClCN_{(S)}$ and $BrCN_{(S)}$.

3.2 *The polar HCN structural analog*

The renormalization description obtained for the polar structure of $HCN_{(S)}$ was assumed (see discussion in Sect. 2.3). This structure is shown in Fig. 1b. In accord with the investigation of the non-polar structure, both the *14mm* tetragonal (Fig. 3a) and the *Imm* orthorombic (Fig. 3b) structures were optimized. For the

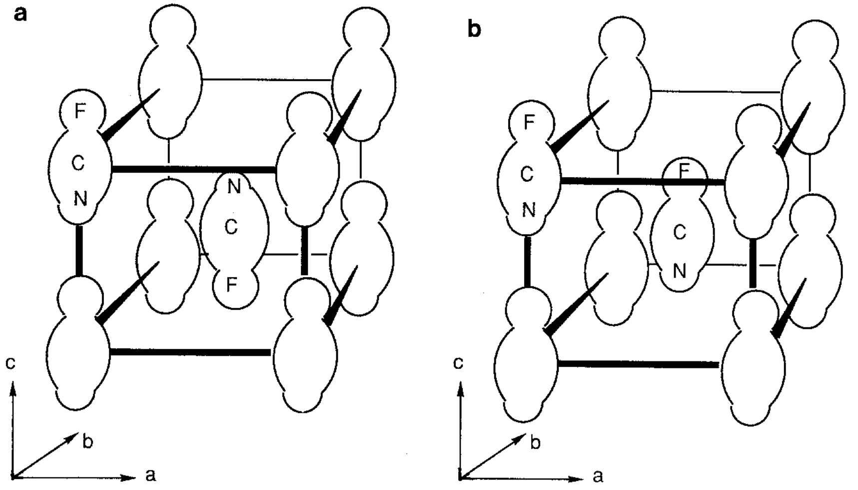
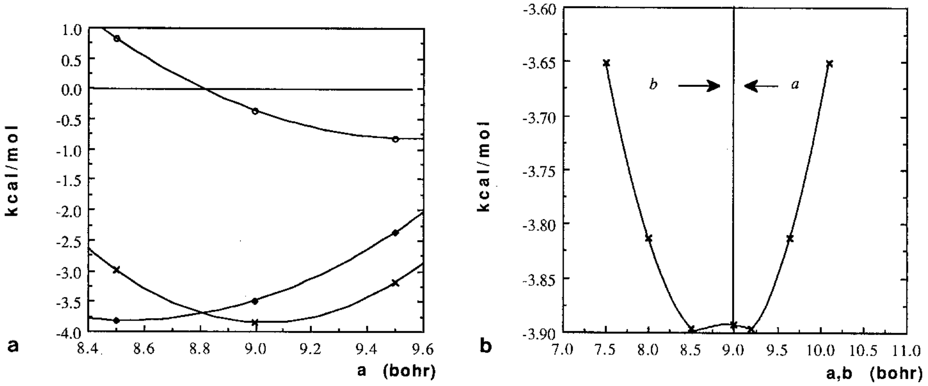


Fig. 1a, b. The non-polar and polar structures are depicted in **Fig. 1a** and **Fig. 1b**, respectively. $a = b$ corresponds to the tetragonal structures *P4/nmm* and *I4mm*, while $a \neq b$ corresponds to the orthorombic structures *Pmmn* and *Imm*, respectively



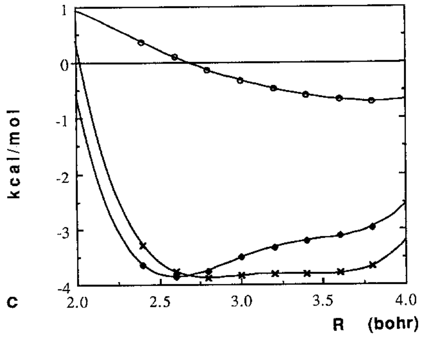


Fig. 2a, c. The potential energy surface for the non-polar arrangement is displayed. **Figure 2a** shows the decomposition of the lattice energy to dispersive and non-dispersive (HF-SCCF + Pauli repulsion) contributions close to the optimal tetragonal structure. **Figure 2b** shows the orthorombic minimum potential energy curve. **Figure 2c** displays the decomposition of the potential energy curve for a transverse inter-chain geometry change. ○ non-dispersive; ◆ dispersive; × total

Table 1. The parameters for the optimized *Pmmn* structure of $FCN_{(S)}$ are displayed together with the corresponding for $ClCN_{(S)}$[a] and $BrCN_{(S)}$. All values in bohr

	a	*b*	*c*	Z(X)	Z(C)	Z(X)
FCN	9.25	8.50	10.25	0.119–0.163	0.352–0.396	0.564–0.607
ClCN[b]	10.74[a]	7.52	10.85	0.149	0.424	0.624
BrCN[c]	11.38	7.79	10.96	0.144	0.45	0.65

[a] There is a misprint in the text of ref. [3] *a* is given as 5.68 Å in the abstract and 3.684 ± 0.007 Å in the text. The correct value is $a = 5.684 \pm 0.007$ Å.

[b] Ref. [3]

[c] Ref. [4]

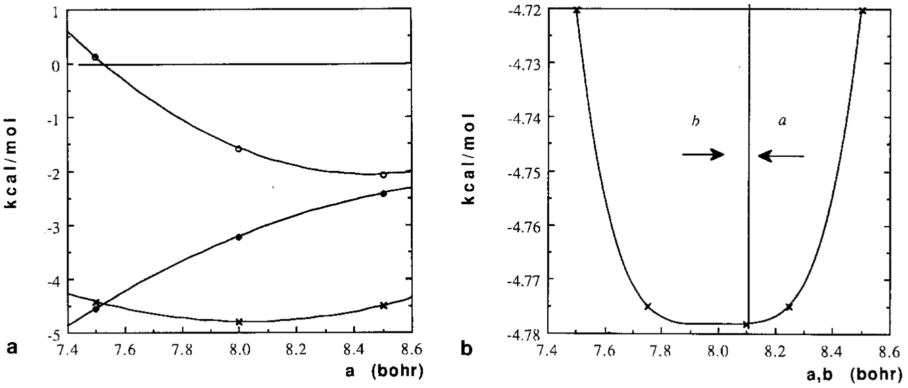


Fig. 3. The potential energy surface for the polar arrangement is displayed. **Figure 3a** is analogous to Fig. 2a and **Fig. 3b** analogous to Fig. 2b. ○ non-dispersive; ◆ dispersive; × total

I4mm space group, the lattice parameters $a = b = 8.1$ bohr and $c = 10.3$ bohr are estimated and a lattice energy of 4.8 kcal/mol is obtained. No asymmetric minimum is found although an orthorombic structure cannot be excluded, due to the shape of the potential energy curve for this degree of freedom (see again Fig. 3b) in conjunction with the neglect of intramolecular electron correlation couplings to the crystal structure.

3.3 On the lattice energy

The lattice energy, for conformations close to the optimal structures, was decomposed into dispersive and non-dispersive contributions (see Fig. 2a and 3a). While the dispersive contribution is found to be fairly similar for the two proposed structures, the non-dispersive contribution is ≈ 1 kcal/mol greater for the polar structure.

Table 2. Δ is the difference between the expected X...N distance from the atomic van der Waals radii[a] and the distance obtained. X is F, Cl, Br, H and I. Values in parentheses are the dipole moments in the solids. All values in atomic units

	Δ	$\lvert\mu\rvert$g, obs	μ_{calc}
FCN	− 0.3[b]	0.846	− 0.697[h], $(-0.945^{\text{nonpolar}}, -1.07^{\text{polar}})$[i]
ClCN	0.8[c]	1.09	–
BrCN	1.1[d]	1.15	–
HCN	1.1[e]	1.174	1.168[i], 1.29[j], (1.73^{nonpolar})[j], (1.89^{polar})[k]
ICN	1.5[f]	1.45	–

[a] Ref. [18], [b] present work, [c] ref. [3], [d] ref. [4], [e] ref. [12], [f] ref. [5], [g] ref. [2], [h] present work, [i] ref. [19], [j] ref. [6], [k] ref. [9].

3.4 On the crystallization mechanism

A decomposition of the lattice energy in terms of intra- and inter-chain contributions was performed by dissociating the crystal into infinite chains. The intermolecular distance was found to increase by less than 0.05 bohr and inter-chain lattice energy contributions of 4.3 and 3.4 kcal/mol are obtained for the polar and non-polar structures, respectively. Hence, the intra-chain contribution to the lattice energy amounts to 10–13% of the total binding in solid FCN. This is in contrast to the 73% and 95% obtained for solid HCN [7, 9] and solid HF [9], respectively. Furthermore, the inter-chain interaction for solid HF was found to be of similar magnitude (0.4–0.5 kcal/mol [9]) as that obtained for the intra-chain interaction for solid FCN (0.5 kcal/mol). This suggests similar melting points, but while $HF_{(S)}$ decomposes into chains, $FCN_{(S)}$ decomposes into sheets. This is supported by experiment, since the − 83°C melting point of $HF_{(S)}$ is almost identical to that of $FCN_{(S)}$.

The above analogy with $HF_{(S)}$ works for the non-polar FCN structure but not for the polar, since the intra-sheet interactions are attractive in the case of the former but repulsive in the case of the latter.

3.5 Some structural considerations

The apparent anomalously short intermolecular distances along the cyanogen halide chains has been an issue of discussion (see [3] and references therein). The general consensus is that this results from the electronically depleted and polarized halogen atom, Cl < Br < I. The present study is able to complete this picture by producing results for $FCN_{(S)}$, were it a $HCN_{(S)}$ or $ClCN_{(S)}$ structural analog.

In Table 2, the difference between the expected intermolecular distances along the chains obtained from the corresponding atomic van der Waals radii and the values for the FCN, ClCN and BrCN, HCN and ICN solids are displayed. The signs and the magnitudes of the discrepancies are correlated to the molecular dipole moments (negative sign is electrons shifted towards X). Properties to note in particular are:

(a) FCN is the only molecule with excess of electrons on X and accordingly, its crystal structure stands out as the only structure with X...N distance larger than expected from the atomic van der Waals radii. This is due to the lone-pair on nitrogen being attracted to X in all cases but X = F. A secondary consequence of this difference is that the unit cell shrinks in *a* and *b* (see Table 1).

(b) $HCN_{(S)}$ does not stand out in the series, which emphasises the similarities between hydrogen bonded and non-hydrogen bonded solids. What makes the hydrogen bond unique is rather its strength, which in turn is a result of the proximity of the ligand lone pair to the H nucleus. This interpretation is in accord with that of Umeyama and Morokuma for the hydrogen bonding in $(H_2O)_2$ and $(HF)_2$ [20].

(c) The gas phase molecular dipole moments are only indicative of the general trend, since the dipole moments in the solid are significantly larger (values in parentheses in Table 2).

4 Conclusion

Two structural candidates of solid FCN have been determined, being $HCN_{(S)}$ and $ClCN_{(S)}$ analogs, respectively.

The structures of solid FCN stand out from the rest in that the intermolecular distance in the chains is greater than what is expected from the van der Waals radii of atomic fluorine and nitrogen. For all other halides the opposite is observed. This effect is explained by the excess of electrons on fluorine. In the cases of the other cyanogen halides the electrons are polarized towards the cyanide.

Acknowledgements. I wish to dedicate this work to Professor Inga Fischer–Hjalmars on the occasion of her 75th birthday in 1993.

The first time I saw Inga was in Stockholm 10 years ago. Then an undergraduate student attending a doctoral dissertation at the Department of Theoretical Physics, I saw this glowing woman at the reception. I asked a person close to me: "Who is that fascinating woman". "Well, Inga of course" came the answer. Later as graduate student at the very same department, I had the privilege to learn to know the person and scientist Inga, and I was not disappointed!

I have met the *person* Inga only occasionally since I left Stockholm in 1989, while the *scientist* Inga is with me much more frequently. Just to give one example: I recently addressed the structure of solid hydrogen peroxide [17], which led me to look up an experimental paper published in the Journal of Chemical Physics. As it happened, Inga had a paper in that very same issue [21]. The subject of that formal paper was to investigate the validity of the inherent approximation in the ZDO method. Such efforts appeal strongly to me and are of great importance to my research. Hence, I find in Inga a continuous source of inspiration and support.

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