Effect of the Crystalline Environment on Molecular Geometries – an *ab initio* Study of Cyanamide[#]

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The *ab initio* geometry of cyanamide in the gaseous and the solid states has been optimized utilizing the analytical energy gradients. Atomic charges from population analyses have been used to simulate crystal field effects. The optimized geometry is in good agreement with experimental findings. The results imply that the point-charge model is successful in describing the crystal field effects on the internal geometry for molecules involved in networks of medium-long hydrogen bonds in the solid state.

The geometries of molecules in the solid state are often different from the geometries of isolated molecules, especially when intermolecular hydrogen bonds are formed. In order to represent crystal field effects in *ab initio* calculations on cyanoformamide, a model based upon net atomic point charges in positions determined by crystal structure analysis was introduced.[1] The geometry of the molecule was optimized utilizing the analytical energy gradients.[2] A double-zeta basis set was applied. Convincing correspondence between calculated and experimental geometries was obtained. The results showed that the point-charge model and the automatic refinement procedure were applicable at least to systems forming planar sheets or chains of hydrogen-bonded molecules in the crystal. Another advantage of the point-charge model is the small increase in computing time compared to that for a free molecule, making it a useful alternative to the practice of applying empirical corrections to *ab initio* geometries of isolated molecules when comparing with experimental solid state geometries.

The geometry of the cyanamide molecule has previously been optimized by *ab initio* methods applying different basis sets,[3–6] and the structure has been studied by microwave spectroscopy[7,8] and the crystal structure determined by single-crystal neutron diffraction techniques.[9] The geometry of the free molecule differs significantly from that of the molecule in the crystal, in which the molecules form a three-dimensional hydrogen-bond network. Point-charge model calculations for cyanamide are hereby presented. Cyanamide is also a molecule for which the introduction of polarization functions is important for obtaining a reasonable *ab initio* structure.[3]

Methods and results

The computational details are as given in Ref. 1, except for a convergence criterion of 0.0001 Å. A double-zeta basis set [(7*s*3*p*/4*s*) contracted to (4*s*2*p*/2*s*)] with polarization functions for the non-hydrogen atoms[10,11] and with scale factor of $(1.2)^2$ for the exponents of hydrogen[12] was used. The calculations were carried out using the program MOLFORC,[13] a gradient program based on MOLECULE.[14]

First, the geometry of the free molecule was optimized. Cyanamide crystallizes in space group *Pbca* with eight molecules in the unit cell, the molecular symmetry is C_1. One molecule is hydrogen-bonded to four neighbours (see Fig. 1) (the N(H1)···N and the N(H2)···N distances are

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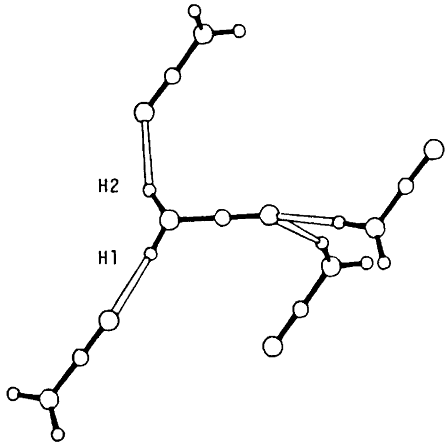

Fig. 1. The cyanamide molecule and its hydrogen bonded neighbours.

3.025 and 3.046 Å, respectively). All twelve molecules with their carbon atom less than 6 Å away from the carbon atom of the central molecule were included in order to simulate the crystal field (cry.f.) in the *ab initio* calculations. Similar calculations with only the four hydrogen-bonded neighbours included were performed in order to examine the hydrogen-bonding (hydr.b.) effects separately. Finally, a double-zeta basis set was applied in the crystal field model. The point-charge–point-charge Coulombic interaction energy terms are not included in the calculated energies. The geometry refinement (by the energy gradient method) was observed to be critically dependent upon the point-charge values. The initial values taken from the population analysis for the isolated molecule were replaced with the values calculated for the point-charge model prior to refinement. In order to obtain self consistency the point-charge values were replaced with those obtained in an iterative optimization procedure.

The geometrical parameters (named as in Ref. 3, Table 1) for the free molecule and the molecule in the solid state are listed in Tables 1 and 2, respectively. The net charges are given in Table 3.

Discussion

The *ab initio* calculations give the molecular geometry of a rigid molecule in an energy minimum. Previous studies on the free molecule and the geometries obtained with different basis sets are summarized in Ref. 5. It has been demonstrated that inclusion of polarization functions (at least) on the amino nitrogen atom is necessary in order to obtain a non-planar amino group.[3] Our double-zeta basis set including polarization functions for the heavy atoms is intermediate between the 4-31G* and the 6-31G* basis sets.[3,5] The optimized geometries derived using all three basis sets are listed in Table 1. The energy minimum is shallow and the final geometries may also be dependent on the convergence criterion.

The experimental parameters for the free molecule are not easily determined as the molecule undergoes large amplitude vibration.[8] The non-planarity of the amino group was established by

Table 1. Geometrical parameters for the free cyanamide molecule (named as in Ref. 3, Table 1).

	ab initio Basis set			Exp. results	
	DZ+P[a]	4-31G*[b]	6-31G*[c]	Ref. 7	Ref. 8
r(NH)/Å	1.001	0.998	0.998	1.001	1.008 (constr.)
r(N−C)/Å	1.349	1.340	1.343	1.346	
r(N≡C)/Å	1.135	1.135	1.138	1.160	1.165 (ass.)
∠HNH/°	111.5	113.5	113.1	113.5	112.8
∠CNH/°	112.9	115.0	114.5	115.6	113.0
Θ(NCN)/°	1.6	2.0	1.8	0 (ass.)	5.2
Θ_{inv}/°	46.3	39.6	41.3	38.0	45.0
energy (+147)/Hartree	−0.78621	−0.76458	−0.90866		
μ/Debye	4.36	4.58	4.59	4.32	4.25 (see 8)

[a]This work. [b]Ref. 3. [c]Ref. 5.

Table 2. Geometrical parameters for cyanamide influenced by neighbours (see text) and in the solid state.

	ab initio Basis set			Exp. results[d]	
	cry.f.[a] DZ+P	hydr.b.[b] DZ+P	cry.f.[c] DZ	100 K	298 K
r(NH1)/(Å)	1.004	1.005	0.999	1.006	1.002
r(NH2)/Å	1.005	1.003	0.999	1.006	1.024
r(N−C)/Å	1.319	1.324	1.321	1.319	1.320
τ(C≡N)/Å	1.143	1.141	1.151	1.175	1.174
∠HNH/°	118.8	118.4	118.8	120.8	120.4
∠CNH1/°	120.2	118.6	120.9	120.0	120.5
∠CNH2/°	118.8	116.9	120.1	117.8	118.4
Θ(NCN)/°	1.5	1.9	0.2	1.5	1.1
Θ_{inv}/°	14.6	24.6	4.9	12.4	8.4
energy (+147)/Hartree	−0.84061	−0.83441	1.24702		

[a]12 Neighbours. [b]4 Neighbours. [c]12 Neighbours. [d]Ref. 9.

Table 3. Mulliken charge densities.

Atom	Basis set				
	Ref. 6	This work			
	isol. 6-31G*	isol. DZ+P	cry.f DZ+P	hydr.b. DZ+P	cry.f. DZ
N(amino)	−0.875	−0.771	−0.827	−0.820	−0.895
N(cyano)	−0.444	−0.329	−0.524	−0.503	−0.374
C	0.502	0.375	0.493	0.480	0.439
H1	0.408	0.363	0.425	0.427	0.414
H2	0.408	0.363	0.433	0.416	0.416

microwave spectroscopy.[7] Whereas a linear N−C−N geometry was assumed in Ref. 7, the semi-rigid bender model treatment[8] indicates a non-linear N−C−N and different r_s structures for different isotopic species. The results are consistent with those of Ref. 7 but yield structural parameters for the energy minimum position as well. However, the carbon−nitrogen triple bond was not refined, and the nitrogen−hydrogen bond length was restricted in order to reduce the number of parameters. The experimental values are included in Table 1.

The bond parameters are reasonably close to the experimental values, except for the carbon−nitrogen triple bond, which is underestimated by calculations of this type (Ref. 5, p. 838) (our calculation on a free molecule was performed in order to eliminate effects caused by different basis sets when comparing the free molecule with the molecule in the solid state).

The neutron diffraction data were collected at room temperature and at low temperatures (100 K). The bond distances to terminal atoms, as well as the bond distance between carbon and the amino nitrogen have been corrected for thermal vibrations assuming riding motion.[15] The derived molecular geometries are not significantly different at the two temperatures, except for the flatness of the amino group (Table 2). The neutron diffraction refinement gives the nuclear positions and harmonic thermal vibration parameters. It is reasonable (on the basis of extrapolation to $T = 0$ K) to expect a somewhat more pyramidal amino group for a static molecule. The amino group is slightly asymmetric and the molecule has C_1 symmetry in the crystal.

The positional parameters from the least-squares refinement of the low-temperature neutron diffraction data were used in the point −charge model calculations. The agreement between the optimized geometry of the crystal field model and the experimental geometry is convincing, and even the asymmetry of the amino group is qualitatively correct (Table 2). It is evident from the simple point-charge model that the main source of energy stabilization in the solid is hydrogen-bond formation. The energy difference between a free molecule and the hydrogen-bonded model is 126.5 kJ mol^{-1} (i.e., 63.2 kJ mol^{-1} for each hydrogen bond). The influence of the other neighbouring molecules (corresponding to a further decrease in energy of 16.3 kJ mol^{-1}) is nevertheless of importance for the amino group bending. The double-zeta basis set also reproduces the experimental solid state findings quite satisfactorily, except for a less pyramidal amino group. However, this basis set gives, as mentioned earlier, a planar free molecule.[3]

The main differences in the calculated geometries between a free molecule and the molecule in the solid state (the first columns in Table 1 and 2, respectively) are a less pyramidal amino group ($\Delta\Theta_{inv}$ = 31.7°), a shorter amino nitrogen−carbon bond (Δ = 0.030 Å), and a longer cyano nitrogen−carbon bond (Δ = 0.008 Å) for the latter. All experimental findings are quantitatively confirmed by the present calculations. In accordance with the findings for cyanoformamide,[1] the population analysis (Table 3) shows that the molecule becomes more polarized in the solid state.

The point-charge model has been frequently applied in theoretical electron density calculations (see Refs. 16 and 17 and references therein).An early study of the internal geometry of bound molecules applying the model is a calculation of the conformation of the oxonium ion in solids.[18] The introduction of the analytical energy gradient calculation[2] has made geometry optimization more or less automatic compared to the time-consuming and rather complicated procedure of earlier days. The results presented provide an example showing that the point charge model is successful in describing crystal field effects on the internal geometry of molecules involved in a network of medium-long hydrogen bonds in the solid state.

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