

A Comparative *ab initio* Study of the Dicyanomethanide, Cyanonitromethanide, Dicyanamide and Cyanonitramide Anions

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Results from geometry optimizations by use of *ab initio* methods and a double zeta basis set give results in good accordance with experimental findings for these four systems. The agreement in the trends when comparing effects of substitution is excellent. Neither optimization with a minimal basis nor MINDO/3 calculations reproduce geometries for systems like the present ones satisfactorily. The anion bond parameters are discussed in terms of qualitative bond concepts.

The structures of the dicyanomethanide (A), the cyanonitromethanide (B), the dicyanamide (C), and the cyanonitramide (D) anions have been determined in our laboratory by low temperature single crystal X-ray studies of the potassium salts.¹ The cyano as well as the nitro group are recognized as powerful electron withdrawing substituents thereby stabilizing the anions. All four systems are found to be essentially planar and they are therefore convenient for a study of the influence of the cyano and nitro group on the adjacent π -systems and *vice versa*. Furthermore, differences in structural parameters within the two pairs of isoelectronic ions demonstrate the influence of the nitrogen lone pair electrons as compared with those of the C—H bond.

The anion geometries as determined in the solid state are to some extent influenced by coordination forces and packing effects. *Ab initio* calculations may give information about structures of isolated anions. In the present paper standard calculations by use of the program MOLECULE² is presented. The cal-

culations were carried out in order to see how well the experimental geometries were reproduced. A recent account on *ab initio* calculations on anions may be found in Ref. 3 and references therein. References to structural findings relevant to the present species will mainly be given in the presentation of the crystal structures.¹

COMPUTATIONAL DETAILS AND GEOMETRY OPTIMIZING PROCEDURES

The calculations were performed on a CYBER-74 with the program MOLECULE² which solves the Roothaan-Hall equations for a Gaussian type basis. All results were calculated with a (7s3p/4s) basis⁴ contracted to (4,2/2). A scale factor of 1.2 was used for the exponents of the hydrogen basis set.^{5,6}

The symmetry requirements were C_{2v} for $\text{CH}(\text{CN})_2^-$ (A) and $\text{N}(\text{CN})_2^-$ (C), and C_s for $\text{CH}(\text{CN})(\text{NO}_2)^-$ (B) and $\text{N}(\text{CN})(\text{NO}_2)^-$ (D). The C—H distance was optimized in (A) and the same value was used for (B). All angles of the nitro groups were given the value 120° and both N—O bond lengths of one nitro group were kept equal. For the initial models experimentally determined bond length and bond angle values were applied, except for C—H for A (1.09 Å), the central angles for A and C (120°), and the cyano legs which were assumed to be linear. First the bonds of the cyano legs were optimized simultaneously. Then the C—H bond was refined for A. For B and D, the N—O bond and the bond between the central atom and the nitro group were optimized. Finally the central bond angle and the bending

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Table 1. Total energies, atomic and overlap populations.

CH(CN) ₂ ⁻ (A)			N(CN) ₂ ⁻ (C)		
Energy: -222.78937 a.u.			Energy: -238.75600 a.u.		
Atomic populations			Atomic populations		
	Gross	π		Gross	π
N1	7.467	1.312	N1	7.431	1.262
C1	6.031	0.880	N3	7.851	1.631
C3	6.183	1.614	C1	5.644	0.922
H	0.820				
Overlap populations			Overlap populations		
	Gross	π		Gross	π
N1-C1	1.587	0.470	N1-C1	1.597	0.468
C1-C3	0.724	0.097	C1-N3	0.724	0.105
C3-H	0.814				
CH(CN)(NO ₂) ⁻ (B)			N(CN)(NO ₂) ⁻ (D)		
Energy: -334.31507 a.u.			Energy: -350.25359 a.u.		
Atomic populations			Atomic populations		
	Gross	π		Gross	π
O1	8.489	1.676	O1	8.459	1.613
O2	8.510	1.684	O2	8.448	1.600
N1	7.400	1.217	N1	7.370	1.220
N2	6.849	1.084	N2	6.579	1.080
C1	6.072	0.901	N3	7.531	1.565
C2	5.899	1.437	C1	5.613	0.923
H	0.786				
Overlap populations			Overlap populations		
	Gross	π		Gross	π
N1-C1	1.512	0.498	N1-C1	1.594	0.480
C1-C2	0.322	0.046	C1-N3	0.392	0.087
C2-N2	0.642	0.210	N3-N2	0.468	0.139
N2-O1	0.367	0.170	N2-O1	0.408	0.190
N2-O2	0.288	0.162	N2-O2	0.448	0.192
C2-H	0.814				

of the cyano groups were adjusted. In every case the coupling between two parameters was included by assuming the energy to be a second order degree polynomial in the parameters and computing six points on the energy surface. The coupling was small in most cases.

RESULTS AND DISCUSSION

The total energies of the geometry optimization procedures and results of Mulliken population analyses are listed in Table 1. All occupied MO's are bound for the four anions. According to Koopmans' theorem, in which the ionization potential is approximated as the energy of the highest occupied orbital, the ionization potentials are 2.39, 3.68, 3.79, and 5.01 eV for A, B, C, and D, respectively. For all species these MO's are π orbitals with large net population on the central atom. The geometries are presented in Fig. 1, where experimental results in parentheses and the numbering of atoms also are given. As the strict symmetry of the anions in the crystalline phase is C_1 , mean values are listed for the dicyano-substituted anions, the values of the C-C≡N angles have been ob-

tained by projecting the atoms into the least-squares planes of the anions, and the small twists of the nitro groups have been neglected. The parameters of the high angle X-ray refinements ($\sin \theta/\lambda > 0.60 - 0.65 \text{ \AA}^{-1}$) have been applied, the largest difference between "equivalent" bonds is 0.005 Å, and the estimated standard deviations in bond length values (excluding hydrogen) are 0.002 Å or less.

The anion geometries of the *ab initio* study are in good accordance with the X-ray results (Fig. 1). Bond lengths (neglecting C-H) and bond angles show discrepancies smaller than 0.02 Å and 5°, respectively. The agreement in the trends when comparing the effects of substitution is excellent except for the N-C≡N angles in the amide anions. According to the theoretical calculations, the introduction of a nitro group should result in an increased bending of the cyano leg. The X-ray results show the opposite, however. The other differences between the experimental and calculated shifts are 0.005 Å or less for comparable bond lengths and less than 1° for the central angles. It must be concluded that the applied double zeta basis set seems to give a satisfactory description of the structural variations within the present set of anions. Furthermore, the coordination forces and packing effects in the crystals do not seem to alter the anion geometries seriously.

Geometries resulting from *ab initio* calculations using minimal basis sets are frequently reported in the literature. For systems analogous to those presented, a warning should be given. In a theoretical study of nitromethane and its anion,⁷ a minimal basis set was used to establish an optimum geometry for a planar

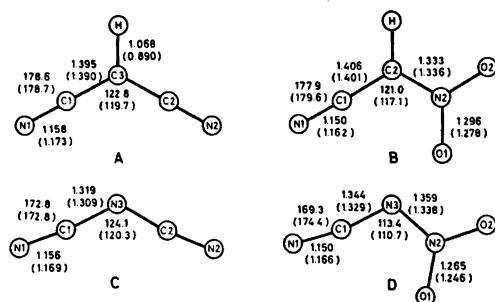


Fig. 1. Anion geometries. (Å and °, experimental values in parentheses.)

anion, even though the authors seemed to be well aware of the pitfalls in this procedure. The resulting geometry was unreasonable as compared with our findings for cyanonitromethanide (B).^{*} Accordingly the geometry of the nitromethanide anion was reoptimized with the present basis set. The results were as follows (values of Ref. 7 in parentheses): N—O = 1.331 (1.228) Å C—N = 1.298 (1.397) Å, C—H = 1.068 (1.090) Å, O—N—O = 120.3 (121)°. The total energy for the anion was 53.1 kJ/mol less for the optimal geometry than for the geometry of Ref. 7 calculated with the present basis set.

The semiempirical MINDO/3 program has recently become readily available.⁸ The parameters for C, H, O, and N have been successfully tested on a large number of species.⁹ The authors state, however, that for the bonds between atoms with lone pairs of electrons, the calculated values are much too small and that for nitriles the results of MINDO/3 are inferior to those of MINDO/2.⁹ Nevertheless, MINDO/3 calculations were carried out in order to see how well the geometries of the present anions were reproduced. Except for the somewhat large values for the central angles [129° for (A) and 127° for (B)], the geometries of the methanides were satisfactory. For the amides the calculations gave reasonable values for the bending of the cyano legs. However, the central angles were seriously in error [153° for (C) and 131° for (D)]. Furthermore, the N—N bond length of cyanonitramide (D) was 1.23 Å and the difference between the

N—O bond lengths of (B) and (D) was not reproduced, both being 1.26 Å. One must conclude that MINDO/3 is not suitable for systems like the present ones.

In the remaining part of the paper the results of the *ab initio* calculations will be discussed in terms of purely qualitative valence bond and electron pair repulsion concepts. In Fig. 2 the distributions of the negative charges of the anions are shown (to the extreme left) together with valence bond structures of importance in describing the resonance stabilized species. The charges are calculated from the gross atomic populations of Table 1 by subtracting the values for neutral atoms. Lacking structural information one might use the following two arguments in order to estimate the relative importance of the canonical forms in describing the ions as resonance hybrids. (1) Nitrogen is more electronegative than carbon, and the unsubstituted amide anion is more stable than the reactive methanide ion; thus A-III and B-III should be of less importance than C-III and D-III. (2) When properly oriented, the nitro group is known as a more powerful electron withdrawing substituent than the cyano group; accordingly B-II and D-II should be more important than B-I and D-I, respectively.

The results of the *ab initio* calculations support this simple description. Within the two isoelectronic pairs the charge density at the central atom is more negative for the amides [by 0.67 and 0.63 e for (A,C) and (B,D), respectively] and the nitro group reduces the charge density [by 0.28 (A,B) and 0.32 e (C,D)]. Furthermore, the gross overlap populations for the bonds between the cyano carbon and the central atoms decrease by introduction of the nitro group. For the bond lengths of the cyano legs one finds a slightly shorter "triple" bond and a somewhat longer bond to the central atom for the methanide as well as for the amide when one cyano group is substituted by the nitro group. The bond lengths of the nitro groups also reflect the relative importance of the canonical forms. The nitronate character of cyanonitromethanide (B-II) is predominant; the N—O bond being rather long and the N—C bond rather short. The observed N—O bond lengths in cyanonitramide (D) are similar to values reported for nitrates

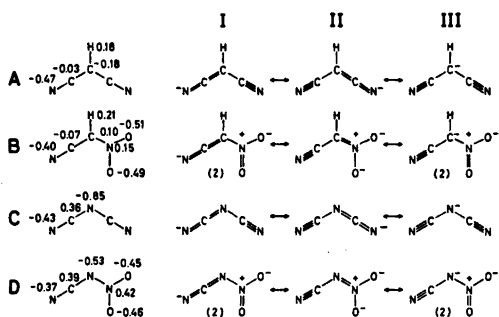


Fig. 2. Atomic charges and valence bond models.

^{*} Added in proof. However, see Ref. 15.

and far shorter than those of the trioxodinitrate anion,¹⁰ where the valence bond structure with a nitrogen nitrogen double bond corresponds most closely to the observed geometry. Accordingly, the N–N bond length of D is 0.074 Å longer than that of trioxodinitrate (X-ray values); the canonical forms having the negative charge at the central atoms contribute thus significantly in the resonance stabilization of the amides. The population analysis shows that although the gross atomic population of the central atom decreases when going from C to D, the π population remains nearly constant.

Finally, some aspects of the bond angle variations will be discussed. We have seen above that introduction of a nitro group causes a lengthening in the bond between the central atom and the other cyano group. The nitro group is also said to be the more electronegative of the two. According to the valence shell electron pair repulsion model the angle between the bonds from the central atoms to the substituents should therefore decrease, in agreement with our findings. A lone pair is said to take up more room on the surface of an atom than a bonding electron pair. The bond lengths to the central atoms of the amide anions indicate more non bonding electrons at the central nitrogen atom in the cyanonitramide (D) than in the dicyanamide (C). This would also tend to decrease the central angle. One would therefore expect a larger decrease in the central angle for the amide than for the methanide anion, when the nitro group replaces one of the cyano groups. The bond angle values support such arguments in contrast to results from the population analysis.

The influence of the lone pair electrons of the central nitrogen atom compared with that of the bonding electrons of the carbon hydrogen bond can be seen by comparing the bending of the cyano legs. Non linear R–C \equiv N arrangements are well known and have been explained in different ways.^{11–13} An *ab initio* study has also recently been published.¹⁴ According to Ref. 13 the sigma lone pair electrons can interact with the in-plane component of the carbon nitrogen multiple bond. If this interaction is bonding, a bend of the π system towards the lone pair will be favoured in order to increase the interaction. Although the

argumentation may be questioned, it predicts non-linearity of the cyano leg in the amide anions, in agreement with our findings. The *ab initio* calculations also give non linear C–C \equiv N arrangements. However, the deviations from linearity are small in these cases. Effects causing non linear C–C \equiv N groups are extensively discussed in Ref. 12.

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REFERENCES

1. Klewe, B. and Tjelta, E. *To be submitted for publication in Acta Chem. Scand. A.*
2. Almlöf, J. USIP rep. 72–09, University of Stockholm, Stockholm 1972.
3. Williams, J. E., Jr. and Streitwieser, A., Jr. *J. Am. Chem. Soc.* 97 (1975) 2634.
4. Roos, B. and Siegbahn, P. *Theor. Chim. Acta* 17 (1970) 209.
5. Huzinaga, S. *J. Chem. Phys.* 42 (1965) 1293.
6. Dunning, T. H., Jr. *J. Chem. Phys.* 53 (1970) 2823.
7. Murrell, J. N., Vidal, B. and Guest, M. F. *J. Chem. Soc. Faraday Trans. 2*, 71 (1975) 1577.
8. Dewar, M. J. S., Metiu, H., Student, P. J., Brown, A., Bingham, R. C., Lo, D. H., Ramsden, C. A., Killmar, H., Weiner, P. and Bischof, P. K. *MINDO/3; Modified Intermediate Neglect of Differential Overlap*, Program 279, Quantum Chemistry Program Exchange, Indiana University, 1975.
9. Bingham, R. C., Dewar, M. J. S. and Lo, D. H. *J. Am. Chem. Soc.* 97 (1975) 1302.
10. Hope, H. and Sequeira, M. R. *Inorg. Chem.* 12 (1973) 286.
11. Hartman, A. and Hirshfeld, F. L. *Acta Crystallogr.* 20 (1966) 80.
12. Matthews, D. A., Swanson, J., Mueller, M. H. and Stucky, G. D. *J. Am. Chem. Soc.* 93 (1971) 5945.
13. Lee, P. L., Cohn, K. and Schwendeman, R. N. *Inorg. Chem.* 11 (1972) 1917.
14. Howell, J. M., Rossi, A. R. and Bissell, R. *Chem. Phys. Lett.* 39 (1976) 312.
15. Mezey, P. G., Kresge, A. J. and Csizmadia, I. G. *Can. J. Chem.* 54 (1976) 2526.

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