

Structural Criteria for the Rational Design of Selective Ligands: Convergent Hydrogen Bonding Sites for the Nitrate Anion

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Abstract: A large number of crystal structures are analyzed to characterize the structural aspects of hydrogen bonding interactions with the NO₃⁻ anion. Further insight is provided by the use of electronic structure calculations to determine stable geometries and interaction energies for NO₃⁻ complexes with several simple hydrogen bond donor groups, including water, methanol, *N*-methylformamide, and methane. The results establish the existence of a clear set of structural criteria for the rational design of molecular receptors that complex the NO₃⁻ anion through hydrogen bonding interactions.

Introduction

Anion complexation by synthetic host molecules has become an important theme in supramolecular chemistry.¹ One of the key challenges is the design of hosts that recognize specific anions, overcoming the normal bias selectivity that exists in pure solution or in ion partitioning where bias is dictated by solvation effects dependent upon anion properties such as basicity² and charge density.³ A successful approach for preparing molecules that coordinate with anions has been to add hydrogen bond donor groups, D–H, to an organic scaffold to yield receptors that interact with anions through hydrogen bonding. Hosts containing a variety of D–H groups have been

investigated. Recent examples include amides,⁴ thioamides,⁵ sulfonamides,⁶ amines,⁷ pyrroles,⁸ imidazolium cations,⁹ ureas,¹⁰ thioureas,¹¹ and guanidinium cations.¹²

Because hydrogen bonds are directional, it should be possible to design hosts with shaped cavities that are capable of

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- (1) (a) *Supramolecular Chemistry of Anions*; Bianchi, A., Bowman-James, K., García-España, E., Eds.; Wiley-VHC: New York, 1997. (b) Schmidtchen, F. P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1609–1646. (c) Gale, P. A. *Coord. Chem. Rev.* **2000**, *199*, 181–233. (d) Gale, P. A. *Coord. Chem. Rev.* **2001**, *213*, 79–128. (e) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486–516. (f) Fitzmaurice, R. J.; Kyne, G. M.; Douheret, D.; Kilburn, J. D. *J. Chem. Soc., Perkin Trans. 1* **2002**, 841–864. (g) McKee, V.; Nelson, J.; Town, R. M. *Chem. Soc. Rev.* **2003**, *32*, 309–325. (h) Martínez-Manez, R.; Saccon, F. *Chem. Rev.* **2003**, *103*, 4419–4476. (i) Suksai, C.; Tuntulani, T. *Chem. Soc. Rev.* **2003**, *32*, 192–202. (j) Choi, K.; Hamilton, A. D. *Coord. Chem. Rev.* **2003**, *240*, 101–110. (k) Lambert, T. N.; Smith, B. D. *Coord. Chem. Rev.* **2003**, *240*, 129–141. (l) Davis, A. P.; Joos, J.-B. *Coord. Chem. Rev.* **2003**, *240*, 143–156. (m) Beer, P. D.; Hayes, E. J. *Coord. Chem. Rev.* **2003**, *240*, 167–189. (n) Gale, P. A. *Coord. Chem. Rev.* **2003**, *240*, 191–221.
- (2) Schneider, H.-J.; Yatsimirsky, A. K. *Principles and Methods in Supramolecular Chemistry*; John Wiley and Sons: Chichester, 2000.
- (3) Moyer, B. A.; Bonnesen, P. V. *Supramolecular Chemistry of Anions*; Bianchi, A., Bowman-James, K., García-España, E., Eds.; Wiley-VHC: New York, 1997; Chapter 1, pp 1–44.

- (4) (a) Choi, K.; Hamilton, A. D. *J. Am. Chem. Soc.* **2003**, *125*, 10 241–10 249. (b) Kang, S. O.; Llinares, J. M.; Powell, D.; VanderVelde, D.; Bowman-James, K. *J. Am. Chem. Soc.* **2003**, *125*, 10 152–10 153. (c) Hossain, M. A.; Kang, S. O.; Powell, D.; Bowman-James, K. *Inorg. Chem.* **2003**, *42*, 1397–1399. (d) Otto, S.; Kubik, S. *J. Am. Chem. Soc.* **2003**, *125*, 7804–7805. (e) Sun, S.-S.; Lees, A. J.; Zavalij, P. Y. *Inorg. Chem.* **2003**, *42*, 3445–3453. (f) Zhang, X.; Guo, L.; Wu, F.-Y.; Jiang, Y.-B. *Org. Lett.* **2003**, *5*, 2667–2670. (g) Camiolo, S.; Gale, P. A.; Hursthouse, M. B.; Light, M. E.; Warriner, C. N. *Tetrahedron Lett.* **2003**, *44*, 1367–1369. (h) Camiolo, S.; Gale, P. A.; Hursthouse, M. B.; Light, M. E. *Org. Biomol. Chem.* **2003**, *1*, 741–744. (i) Bondy, C. R.; Loeb, S. J. *Coord. Chem. Rev.* **2003**, *240*, 77–99.
- (5) (a) Hossain, M. A.; Kang, S. O.; Llinares, J. M.; Powell, D.; Bowman-James, K. *Inorg. Chem.* **2003**, *42*, 5043–5045. (b) Inoue, Y.; Kanbara, T.; Yamamoto, T. *Tetrahedron Lett.* **2003**, *44*, 5167–5169.
- (6) Hettche, F.; Hoffman, R. W. *New. J. Chem.* **2003**, *27*, 172–177.
- (7) (a) Tobey, S. L.; Anslyn, E. V. *J. Am. Chem. Soc.* **2003**, *125*, 10 963–10 970. (b) Morehouse, P.; Hossain, M. A.; Llinares, J. M.; Powell, D.; Bowman-James, K. *Inorg. Chem.* **2003**, *42*, 8131–8133. (c) Llinares, J. M.; Powell, D.; Bowman-James, K. *Coord. Chem. Rev.* **2003**, *240*, 55–57. (d) Farrell, D.; Gloe, K.; Goretzki, G.; McKee, V.; Nelson, J.; Nieuwenhuyzen, M.; Pal, I.; Stephan, H.; Town, R. M.; Wichmann, K. *Dalton Trans.* **2003**, 1961–1968.
- (8) (a) Sessler, J. L.; Dan Pantos, G.; Katayev, E.; Lynch, V. M. *Org. Lett.* **2003**, *5*, 4141–4144. (b) Levitskaia, T. G.; Marquez, M.; Sessler, J. L.; Shriver, J. A.; Vercouter, T.; Moyer, B. A. *Chem. Commun.* **2003**, 2248–2249. (c) Bucher, C.; Zimmerman, R. S.; Lynch, V.; Sessler, J. L. *Chem. Commun.* **2003**, 1646–1647. (d) Sessler, J. L.; An, D.; Cho, W.-S.; Lynch, V. *J. Am. Chem. Soc.* **2003**, *125*, 13 646–13 647. (e) Lee, C.-H.; Na, H.-K.; Yoon, D.-W.; Won, D.-H.; Cho, W.-S.; Lynch, V. M.; Shevchuk, S. V.; Sessler, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 7301–7306. (f) Warriner, C. N.; Gale, P. A.; Light, M. E.; Hursthouse, M. B. *Chem. Commun.* **2003**, 1810–1811. (g) Vega, I. E. D.; Camiolo, P. A.; Hursthouse, M. B.; Light, M. E. *Chem. Commun.* **2003**, 1686–1687. (h) Sessler, J. L.; Camiolo, S.; Gale, P. A. *Coord. Chem. Rev.* **2003**, *240*, 17–55.
- (9) Yun, S.; Ihm, H.; Kim, H. G.; Lee, C.-W.; Indrajit, B.; Oh, K. S.; Gong, Y. J.; Lee, J. W.; Yoon, J.; Lee, H. C.; Kim, K. S. *J. Org. Chem.* **2003**, *68*, 2467–2470.

differentiating between anionic guests with different geometries. Extensive studies of cation coordination chemistry have established that certain structural properties promote more effective and more selective ion receptors.^{2,13} It is generally understood that a successful design will entail positioning convergent D–H groups on a rigid scaffold. However, both the number of D–H groups and the definition of geometric features that constitute D–H convergence are not well defined for most anions. The deliberate design of selective host architecture entails a detailed knowledge of the structural aspects of hydrogen bonding with the guest anion. Yet, surprisingly little attention has been given to this critical facet of receptor design.

Studies of hydrogen bonding in a wide variety of systems suggest that certain geometric features must be present to attain the optimal hydrogen bonding interaction between D–H and the acceptor atom A of the anion.^{14,15} First, for any given hydrogen bond, there is a D–H···A contact distance, d , that will give the strongest interaction. This distance may show significant variation depending on the identity of the D–H, A pair, the presence of other hydrogen bonding groups coordinated to the anion, and the influence of the surrounding medium. Second, hydrogen bonds tend to be linear, that is, the D–H···A angles are near 180°. Linear D–H···A angles are expected for strong hydrogen bonds and can be rationalized by the energetic stabilization that results from orienting the D–H bond dipole to point toward the acceptor atom.¹⁴

The degree of D–H convergence is characterized by d and the D–H···A angle alone when there is no significant directionality at the anion, as is the case with halide ions. This may not be true for anions containing two or more atoms. In a recent communication, we presented crystallographic evidence for the existence of distinct and general oxygen atom acceptor directionalities in both trigonal planar and tetrahedral oxanions.¹⁶ This observation—fully consistent with prior observations of oxygen atom acceptor directionality in weak to moderate hydrogen bonds to ketones, aldehydes, ethers, epoxides, and alcohols¹⁷—suggests a third geometric feature must be considered in the design of receptors for oxyanions; the spatial arrangement of the hydrogen atoms about the oxygen acceptor atoms. This arrangement can be characterized in terms of H···O–X angles and H···O–X–O dihedral angles.

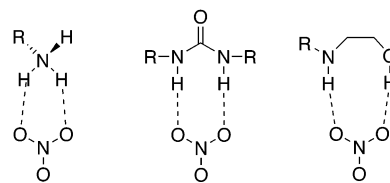


Figure 1. Examples of diprotic hydrogen bonding fragments excluded from the data set.

In this paper, we present a detailed study of the structural aspects of hydrogen bonding interactions with the trigonal planar NO_3^- anion. A large number of crystal structures are analyzed to further characterize these interactions and to investigate the number of D–H contacts per anion. Electronic structure calculations are used to determine stable geometries and interaction energies for NO_3^- complexes with several simple molecules possessing hydrogen bond donor groups including H_2O , methanol (MeOH), *N*-methylformamide (NMF), and CH_4 . Comparisons with experimental data both verify the computational results and firmly establish the nature of the geometric parameters that define optimal D–H interactions for this anion. An electrostatic potential surface reveals that the NO_3^- anion has distinct binding sites for six D–H interactions. Steric considerations explain why this coordination number is not achieved with mono-protic donor groups, which instead tend to form complexes with only three D–H groups. Convergent arrangements for three alcohol O–H donors and three amide N–H donors are presented, providing a basis for the future design of NO_3^- host architectures.

Methods

Experimental structural parameters for intermolecular contacts between the NO_3^- anion and any hydrogen bond donor group, D–H, were retrieved from the November 2002 release (Version 5.24) of the Cambridge Structural Database (CSD) using the QUEST and VISTA programs.¹⁸ Searches were subject to the following general constraints: R-factor less than 0.10, no disorder, and error free. Structures were rejected when the NO_3^- anion was coordinated to a metal ion. The D–H bond lengths were normalized prior to gathering structural data using the default settings in QUEST; that is C–H 1.083 Å, N–H 1.009 Å, and O–H 0.983 Å.

With the above constraints, searches of the CSD were conducted to gather data for comparison with specific structures obtained from electronic structure calculations on complexes of NO_3^- with H_2O , MeOH, NMF, and CH_4 . Data were retrieved for all examples in which the D–H··· ONO_2^- contact distance, d , fell within a specified range: D = O or N, $1.5 \leq d \leq 2.0$ Å; D = C, $1.5 \leq d \leq 2.5$ Å.

In addition, a general search over all D–H groups was performed to retrieve data for NO_3^- anions in which d varied over the range of $1.5 \leq d \leq 3.0$ Å. In this large search, when a D–H hydrogen atom was within 3.0 Å of more than one oxygen atom in the same NO_3^- anion, the shortest contact was retained and other contact(s) were removed from the data such that all D–H groups in the vicinity of the anion were counted only once. In addition, to exclude hydrogen bonding geometries that might be influenced by intramolecular steric factors, structures were rejected if two D–H groups (D = O or N) interacting with the same NO_3^- anion were connected by two or less atoms to form a chelating entity (see Figure 1).

- (10) (a) Sisson, A. L.; Clare, J. P.; Taylor, L. H.; Charmant, J. P. H.; Davis, A. P. *Chem. Commun.* **2003**, 2246–2247. (b) Pratt, M. D.; Beer, P. D. *Polyhedron* **2003**, *22*, 649–653. (c) Dudic, M.; Lhotak, P.; Stilbor, I.; Lang, K.; Proskova, P. *Org. Lett.* **2003**, *5*, 149–152.
- (11) (a) Tumchare, G.; Tuntulani, T.; Coles, S. J.; Hursthouse, M. B.; Kilburn, J. D. *Org. Lett.* **2003**, *26*, 4971–4974. (b) Kondo, S.; Nagamine, M.; Yano, Y. *Tetrahedron Lett.* **2003**, *44*, 8801–8804. (c) Lam, C.-K.; Mak, T. C. W. *Chem. Commun.* **2003**, 2660–2661.
- (12) (a) Tobey, S. L.; Anslyn, E. V. *J. Am. Chem. Soc.* **2003**, *125*, 14 807–14 815. (b) Tobey, S. L.; Jones, B. D.; Anslyn, E. V. *J. Am. Chem. Soc.* **2003**, *125*, 4026–4027. (c) Wiskur, S. L.; Floriano, P. N.; Anslyn, E. V.; McDevitt, J. T. *Angew. Chem., Int. Ed.* **2003**, *42*, 2070–2072. (d) Best, M. D.; Tobey, S. L.; Anslyn, E. V. *Coord. Chem. Rev.* **2003**, *240*, 3–15.
- (13) (a) Hancock, R. D.; Martell, A. E. *Chem. Rev.* **1989**, *89*, 1875–1914. (b) Busch, D. *Chem. Rev.* **1993**, *93*, 847–860. (c) Martell, A. E.; Hancock, R. D. *Metal Complexes in Aqueous Solution*; Fackler, J. F., Jr., Ed.; Plenum Press: New York, 1996. (d) Hay, B. P.; Hancock, R. D. *Coord. Chem. Rev.* **2001**, *212*, 61–78.
- (14) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Truhlar, D. G., Ed.; Oxford University Press: Oxford, 1997.
- (15) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press: Oxford, 1999.
- (16) Hay, B. P.; Dixon, D. A.; Bryan, J. C.; Moyer, B. A. *J. Am. Chem. Soc.* **2002**, *124*, 182–183.
- (17) (a) Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063–5070. (b) Taylor, R.; Kennard, O.; Versichel, W. *J. Am. Chem. Soc.* **1983**, *105*, 5761–5766. (c) Murray-Rust, P.; Glusker, J. P. *J. Am. Chem. Soc.* **1984**, *106*, 1018–1025. (d) Steiner, T.; Kanters, J. A.; Kroon J. *Chem. Commun.* **1996**, 1277–1278. (e) Steiner, T. *Chem. Commun.* **1997**, 727–734.

- (18) (a) Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146–153. (b) Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Smith, J. M.; Watson, D. G. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187–204. (c) Allen, F. H.; Kennard, O. *Chemical Design Automation News* **1993**, *8*, 31–37.

Geometries for **1–6** were optimized by using density functional theory¹⁹ and second-order Møller–Plesset theory (MP2).²⁰ Initial geometries were optimized with the BP86 functional^{21,22} and the DN^{N*} polarized double numerical basis set.²³ Further optimization of the hydrogen bonded structures was done with the hybrid B3LYP functional^{21,24} and a polarized triple- ζ basis set (TZVP).²⁵ The TZVP basis set was augmented (TZVP+) with valence diffuse functions (s for hydrogen, and s and p for C, N, and O) to better describe the electronic charge distribution in anionic complexes with exponents for the additional diffuse functions (atom, α_s , α_p): H, 0.04573; C, 0.04441, 0.02922; N, 0.06035, 0.04073; O, 0.08142, 0.04812. The B3LYP calculations were performed using the NWChem²⁶ and Gaussian 98²⁷ programs. Frequency calculations, done at the B3LYP/TZVP+ level, verified that the optimized geometries were stable points on the potential energy surface. Geometries for **7–10** were optimized at the B3LYP/TZVP level only.

In addition to conventional hydrogen bonds involving two highly electronegative atoms (N or O), we also explored less conventional complexes with a CH group acting as a proton donor. The results of recent studies on neutral and charged clusters indicate that the hybrid B3LYP functional is satisfactory for systems with conventional intra- and intermolecular hydrogen bonds, though the B3LYP stabilization energies are less accurate than those resulting from highly correlated electronic structure calculations.²⁸ The relatively weak hydrogen bonds formed by C–H groups may require an explicit treatment of intermolecular dispersion effects. For this reason, the geometries for **1–6** were optimized at the MP2 level using the augmented correlation consistent double- ζ basis set (aug-cc-pVDZ).²⁹ To eliminate basis set superposition error issues and get the best energies possible at the MP2 level, calculations were done with larger correlation-consistent basis sets to allow extrapolation to the complete basis set limit. Single point

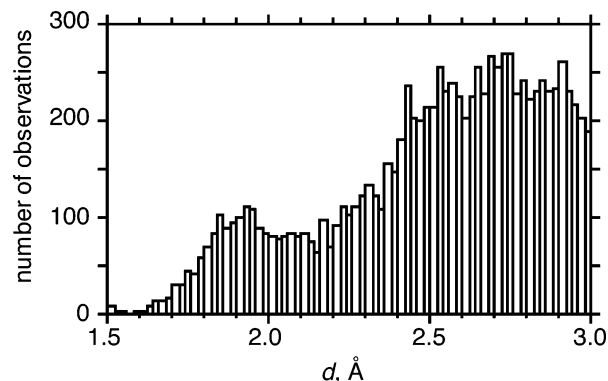


Figure 2. Distribution of CSD H \cdots O distances, d , observed for 10,065 H atoms within 3 Å of at least one O atom in 945 NO $_3^-$ anions.

calculations were carried out with the NWChem program at the MP2/aug-cc-pVTZ and MP2/aug-cc-pVQZ levels at the MP2/aug-cc-pVDZ geometries. The complete basis set (CBS) limit was obtained by extrapolating the total energies, MP2/aug-cc-pVXZ for X = D, T, and Q, of each conformer by using a mixed Gaussian exponential extrapolation.³⁰ We previously have used this approach to predict hydrogen bond energies and conformational energies.³¹

Potential energy surfaces for distortions of selected structural parameters in one (MeOH)NO $_3^-$ complex, **4**, and the (NMF)NO $_3^-$ complex, **5**, were obtained with single-point energies at the B3LYP/TZVP+ level of theory. The structural parameters were the O \cdots H distance, the D–H \cdots O angle (D = O or N), the N–O \cdots H angle, and the O–N–O \cdots H dihedral angle. For each potential energy surface, geometries were generated by variation of the specified structural parameter, keeping all other structural features constant.

Results and Discussion

Structural Features of NO $_3^-$ Hydrogen Bonding Interactions in Crystal Structures. Crystal structure data was used both to evaluate the structural parameters for D–H \cdots ONO $_2^-$ interactions and to determine the average number of D–H contacts per NO $_3^-$ anion. A general search of the CSD was performed to retrieve all examples of hydrogen bonding interactions with NO $_3^-$ anions in which a D–H hydrogen atom was within 1.5 and 3.0 Å distance to at least one NO $_3^-$ oxygen atom. In this large search, chelating structures (see Figure 1) were rejected in order to exclude hydrogen bonds in which geometric features are expected to be influenced by intramolecular constraints imposed by the chelate geometry. The search yielded a total of 10 065 H atoms in contact with 945 NO $_3^-$ anions. A plot of the distribution of the number of contacts as a function of this distance, d , is shown in Figure 2. The distribution is bimodal, with a smaller peak centered at \sim 1.9 Å and a larger peak centered at \sim 2.7 Å. The behavior exhibited in this plot is typical of that expected for a mixture of strong and weak D–H groups.³²

The data were binned in 0.1 Å intervals and statistical analysis of the hydrogen bond structural parameters was performed as a function of d . The results are presented in Table 1. When $d < 2.1$ Å, the majority of the contacts involve D–H groups in which

- (19) (a) Parr R. G.; Yang, W. In *Density Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, 1989. (b) *Density Functional Methods in Chemistry*; Labanowski, J. K., Andzelm, J. W., Eds.; Springer-Verlag: New York, 1991.
- (20) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618–620. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1–10.
- (21) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100.
- (22) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822–8824.
- (23) *MacSpartan Pro User's Guide*; WaveFunction, Inc.: Irvine, California; 2000, <http://www.wavefun.com>.
- (24) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789.
- (25) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560–571.
- (26) (a) Bernholdt, D. E.; Apra, E.; Fruchtl, H. A.; Guest, M. F.; Harrison, R. J.; Kendall, R. A.; Kutteh, R. A.; Long, X.; Nicholas, J. B.; Nichols, J. A.; Taylor, H. L.; Wong, A. T.; Fan, G. I.; Littlefield, R. J.; Nieplocha, J. *Int. J. Quantum Chem. Symp.* **1995**, *29*, 475–483. (b) Harrison, R. J.; Nichols, J. A.; Straatsma, T. P.; Dupuis, M.; Bylaska, E. J.; Fann, G. I.; Windus, T. L.; Apra, E.; Ansell, J.; Bernholdt, D.; Borowski, P.; Clark, T.; Clerc, D.; Dachselt, H.; de Jong, B.; Deegan, M.; Dyall, K.; Elwood, D.; Fruchtl, H.; Glendenning, E.; Gutowski, M.; Hess, A. C.; Jaffe, J.; Johnson, B.; Ju, J.; Kendall, R. A.; Kobayashi, R.; Kutteh, R.; Lin, Z.; Littlefield, R.; Long, X.; Meng, B.; Nieplocha, J.; Niu, S.; Rosing, M.; Sandrone, G.; Stave, M.; Taylor, H.; Thomas, G. van Lenthe, J.; Wolinski, K.; Wong, A.; Zhang, Z. *NWChem, A Computational Chemistry Package for Parallel Computers*, version 4.0.1; William, R., Ed.; Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory: Richland, WA, 99352-0999, USA, 2001.
- (27) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 98*, revision A.4.; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (28) (a) Chandra, A. K.; Nguyen, M. T.; Uchimaru, T.; Zeegers-Huyskens, T. *J. Phys. Chem. A* **1999**, *103*, 8853–8860. (b) Dkhissi, A.; Adamowicz, L.; Maes, G. *J. Phys. Chem. A* **2000**, *104*, 2112–2119. (c) Rak, J.; Skurski, P.; Simons, J.; Gutowski, M. *J. Am. Chem. Soc.* **2001**, *123*, 11 695–11 707. (d) Skurski, P.; Rak, J.; Simons, J.; Gutowski, M. *J. Am. Chem. Soc.* **2001**, *123*, 11073–11074. (e) Kryachko, E. S.; Nguyen, M. T.; Zeegers-Huyskens, T. *J. Phys. Chem. A* **2001**, *105*, 1934–1943. (f) Dabkowska, I.; Rak, J.; Gutowski, M. *J. Phys. Chem. A* **2002**, *106*, 7423–7433.
- (29) (a) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007–1023. (b) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796–6806.

- (30) (a) Peterson, K. A.; Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1994**, *100*, 7410–7415. (b) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1994**, *101*, 8877–8893.
- (31) (a) Vargas, R.; Garza, J.; Dixon, D. A.; Hay, B. P. *J. Am. Chem. Soc.* **2000**, *122*, 4750–4755. (b) Vargas, R.; Garza, J.; Friesner, R. A.; Stern, H.; Hay, B. P.; Dixon, D. A. *J. Phys. Chem. A* **2001**, *105*, 4963–4968. (c) Vargas, R.; Garza, J.; Hay, B. P.; Dixon, D. A. *J. Phys. Chem. A* **2002**, *106*, 3213–3218.
- (32) Steiner, T. *Crystallogr. Rev.* **1996**, *6*, 1–57.

Table 1. Experimental Structural Parameters from the CSD for All H Atom Contacts with NO₃⁻ as a Function of the H···O Distance, *d*^a

<i>d</i>	total no. of D–H contacts	no. of C–H contacts	D–H···O angle (deg)	H···O–N angle (deg)	H···O–N–O dihedral (deg)
1.6 ≤ <i>d</i> < 1.7	52	2	165 ± 11	116 ± 10	0 ± 17
1.7 ≤ <i>d</i> < 1.8	200	1	166 ± 9	115 ± 10	0 ± 25
1.8 ≤ <i>d</i> < 1.9	440	0	164 ± 8	115 ± 11	0 ± 27
1.9 ≤ <i>d</i> < 2.0	492	2	160 ± 9	113 ± 15	0 ± 30
2.0 ≤ <i>d</i> < 2.1	398	19	156 ± 12	112 ± 16	0 ± 30
2.1 ≤ <i>d</i> < 2.2	392	114	152 ± 14	117 ± 21	0 ± 38
2.2 ≤ <i>d</i> < 2.3	530	348	151 ± 15	121 ± 22	0 ± 46
2.3 ≤ <i>d</i> < 2.4	672	577	147 ± 15	121 ± 22	0 ± 48
2.4 ≤ <i>d</i> < 2.5	1028	943	142 ± 16	120 ± 23	0 ± 52
2.5 ≤ <i>d</i> < 2.6	1144	1055	137 ± 17	119 ± 24	0 ± 54
2.6 ≤ <i>d</i> < 2.7	1189	1086	131 ± 18	118 ± 25	0 ± 56
2.7 ≤ <i>d</i> < 2.8	1247	1086	124 ± 19	117 ± 24	0 ± 57
2.8 ≤ <i>d</i> < 2.9	1167	993	120 ± 20	118 ± 25	0 ± 57
2.9 ≤ <i>d</i> < 3.0	1100	906	113 ± 21	118 ± 24	0 ± 58

^a Units: distances in angstroms, angles in degrees. Uncertainties represent one standard deviation from the mean. Values for the H···O–N–O dihedral were calculated assuming that the data were distributed about 0° and using all data in the range of -90.0 < Φ < 90.0°.

D = O or N. Above 2.3 Å, the majority of the contacts are with C–H donor groups. As we reported in a prior communication,¹⁶ at short contact distances, *d* ≤ 2.0 Å, there is evidence for hydrogen bonding directionality in both the donor and the acceptor. The D–H groups show the expected tendency toward a linear D–H···O angle,¹⁴ and the oxygen atom acceptors in the NO₃⁻ anion exhibit a preference for the hydrogen atom to lie in the plane of the anion with a bent H···O–N angle. The directionality becomes less pronounced as *d* becomes longer. This behavior is shown in Table 1 and is graphically illustrated in Figure 3. When *d* < 2.2 Å, the described directionality is clear. However, the angle and dihedral angle distributions noticeably broaden as *d* increases beyond 2.2 Å and become progressively more random as *d* becomes longer.

The bent N–O···H angle and planar O–N–O···H dihedral angles are predicted by the attractive portion of the electrostatic potential for the NO₃⁻ anion.¹⁶ A contour map of the electrostatic potential surface in the plane of NO₃⁻ (Figure 4) reveals the location of minima for the placement of positive charge.^{16,33} There are two minima on either side of the each oxygen atom within the plane of the anion, in other words, at approximately the positions expected for lone pairs from idealized sp² hybrid orbitals. These minima closely correspond to the observed locations of the hydrogen atoms in the crystal structures with short contact distances.

In addition to providing information on hydrogen bonding directionality, the analysis of the CSD data provides some insight into the average number of D–H groups contacting the NO₃⁻ anion. To obtain the desired count, it was necessary to detect H atoms that were in contact with more than one oxygen atom in the same NO₃⁻ anion, in other words, situations that could be described as bifurcated hydrogen bonding, and count these hydrogen atoms only once. If the entire data set was considered, then roughly 25% of the D–H groups contacted two oxygen atoms with *d* < 3.0 Å. In these cases, the shorter contact was retained and the longer contact was excluded from the data set. Dividing the total number of remaining hydrogen

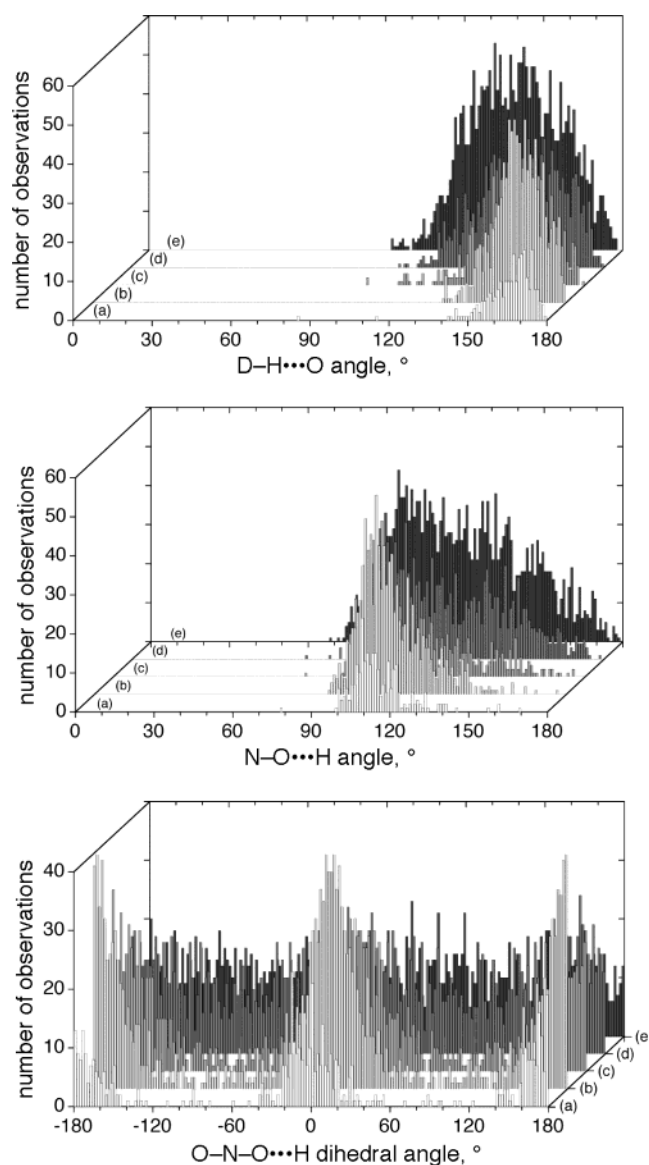


Figure 3. Distributions of CSD structural parameters as a function of *d*: (a) 1.6 ≤ *d* < 1.8; (b) 1.8 ≤ *d* < 2.0; (c) 2.0 ≤ *d* < 2.2; (d) 2.2 ≤ *d* < 2.4; (e) 2.4 ≤ *d* < 2.6 Å.

contacts by the total number of NO₃⁻ anions yields a maximum coordination number of 10.6 D–H per NO₃⁻ anion. The majority of these contacts, however, involve weakly donating C–H groups at relatively long contact distances, many of which are not properly oriented to complement acceptor directionality. If focus is restricted to stronger D–H groups which dominate at the shorter contact distances, primarily O–H and N–H donors, we obtain the following values for D–H per NO₃⁻ as a function of *d*: 2.1 for *d* < 2.2 Å; 2.7 for *d* < 2.3 Å; 3.4 for *d* < 2.4 Å.

Optimized Geometries for Isolated One-to-One Complexes. Electronic structure calculations on isolated complexes further support the existence of an intrinsic directionality at the NO₃⁻ oxygen atom acceptor. Figure 5 shows the stable geometries obtained by geometry optimizations of one-to-one complexes of NO₃⁻ with different D–H groups. All levels of DFT optimizations yield two structures for H₂O, **1** and **2**, two structures for MeOH, **3** and **4**, one structure for NMF, **5**, and one structure for CH₄, **6**. Tables 2–5 present a comparison of

(33) Camaioni, D. M.; Dupuis, M. Bentley, J. *J. Phys. Chem. A* **2003**, *107*, 5778–5788.

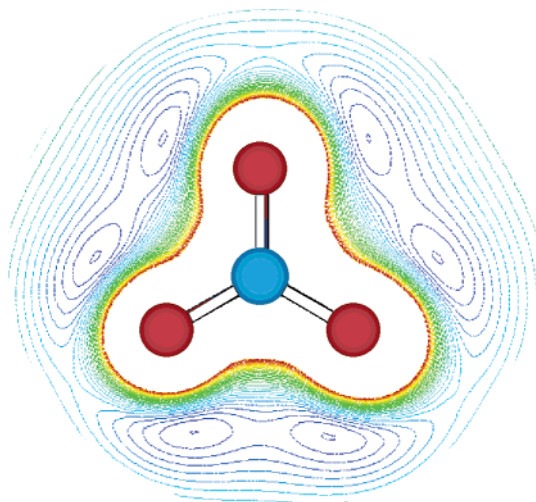


Figure 4. Contour map of the electrostatic potential surface for a positive point charge in the plane of nitrate.¹⁶ Contour lines are spaced at 5 kcal mol⁻¹ intervals. The six equivalent low-energy regions are bound by contours at -165 kcal mol⁻¹.

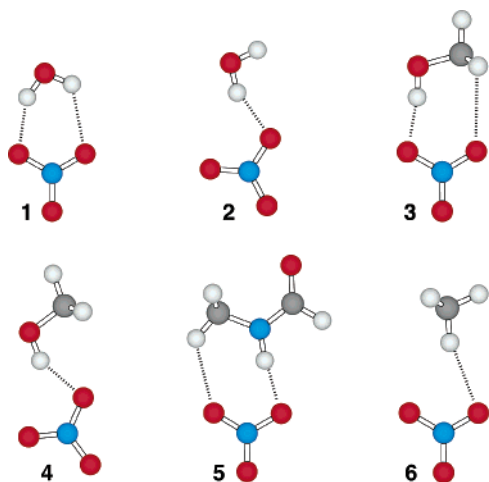


Figure 5. MP2/aug-cc-pVDZ optimized geometries for 1–6.

structural parameters for 1–6 obtained from optimizations at different levels of theory and from evaluation of crystal structure data. The geometries obtained at the different levels of theory are similar, but they do show some variability. For the stronger O–H and N–H donors, the maximum variation in geometric parameters is as follows: d , ± 0.11 Å; D–H \cdots O angle, $\pm 11^\circ$; N–O \cdots H angle, $\pm 12^\circ$; O–N–O \cdots H dihedral angle, $\pm 4^\circ$. The variability is larger for the weaker C–H donors: d , ± 0.33 Å; C–H \cdots O angle, $\pm 34^\circ$; N–O \cdots H angle, $\pm 19^\circ$; O–N–O \cdots H dihedral angle, $\pm 11^\circ$. Surprisingly, the smallest differences are found for the dihedral angles which usually are constrained by the weakest forces.

Five prior theoretical studies also have yielded two geometries for (H₂O)NO₃⁻ complexes, one with two hydrogen bonds and one with a single hydrogen bond. At the Hartree–Fock level of theory, the complex containing two hydrogen bonds is found to have C_{2v} symmetry.^{34–36} However, both DFT^{37,38} and MP2³⁸

calculations find this form to be a transition state and yield a C_s symmetry geometry similar to 1, in which the two hydrogen bonds are asymmetric. All prior studies identified the single hydrogen bond form to have a geometry similar to 2.

Complexes 1, 3, and 5 contain a shorter hydrogen bond to one NO₃⁻ oxygen atom and a longer hydrogen bond to another NO₃⁻ oxygen atom. It is reasonable to assume that the shorter contact represents the stronger interaction in these complexes. Complexes 2, 4, and 6 exhibit only one hydrogen bond interaction. If we compare the geometric features for the strongest hydrogen bonds in 1–6, several trends emerge. In every case, the D–H \cdots O angle is near linear, ranging from 152 to 177°, the N–O \cdots H angle is bent, ranging from 98 to 123°, and the O–N–O \cdots H dihedral angle is near 0° or 180°.

Tables 2–5 also report the average geometric parameters observed in crystal structures containing examples of NO₃⁻ complexes with H₂O, aliphatic alcohols, amides, and aliphatic C–H donors. With the exception of d , there is remarkable agreement between the theoretical and experimental values. The calculated d values are generally shorter than the X-ray distances. This difference is not unexpected. “Gas-phase” calculations on complexes between an anion and a single hydrogen bond donor should yield tighter complexes than observed in condensed phases because (i) hydrogen bonds, which are predominantly electrostatic, are weakened when placed in a dielectric medium, and (ii) a single hydrogen bond interaction polarizes and redistributes the charge on the anion in a different way as compared to the multiple hydrogen bond interactions that are present in solution or crystalline phases. Sharing of charge among multiple D–H partners will lead to weaker interactions with each partner even though the sum of the interactions may be significantly larger than that for an individual D–H group.

The CSD yields 184 examples in which at least one hydrogen atom of H₂O is within 2.0 Å of a NO₃⁻ oxygen atom. There is only one clear occurrence of asymmetric bidentate hydrogen bonding, as in 1, where the short hydrogen bond is 1.84 Å and the long hydrogen bond is 2.51 Å.³⁹ For the rest of these structures there is only a single hydrogen bond between the H₂O molecule and NO₃⁻, as in 2. The average structural parameters observed for these condensed-phase HOH \cdots ONO₂⁻ interactions correspond closely to those calculated for 2.

The CSD yields 37 examples in which the O–H group of an aliphatic alcohol is within 2.0 Å of a NO₃⁻ oxygen atom. As with H₂O, the majority of these examples have a single hydrogen bond to NO₃⁻, that is, they most resemble 4. There are, however, six cases in which a R₂(HO)C–H hydrogen atom interacts with an adjacent NO₃⁻ oxygen atom yielding a chelate structure similar to that observed in 3. As with H₂O, the average geometric parameters observed for ROH \cdots ONO₂⁻ in the solid state are very similar to those calculated for the one-to-one complexes of MeOH \cdots ONO₂⁻, 3 and 4.

Although there are no examples in which the N–H group of an N-alkylformamide is hydrogen bonded to NO₃⁻, the CSD contains 36 examples in which the N–H donor group of an

(34) Howell, J. M.; Sapse, A. M.; Singman, E.; and Snyder, G. J. *Phys. Chem.* **1982**, *86*, 2345–2349.

(35) Shen, M.; Xie, Y.; Schaefer, H. F.; Deakyne, C. A. *J. Chem. Phys.* **1990**, *93*, 3379–3388.

(36) Waterland, M. R.; Stockwell, D.; Kelley, A. M. *J. Chem. Phys.* **2001**, *114*, 6249–6258.

(37) Ebner, C.; Sansone, R.; Probst, M. *Int. J. Quantum Chem.* **1998**, *70*, 877–886.

(38) Wang, X.-B.; Yang, X.; Wang, L.-S.; Nicholas, J. B. *J. Chem. Phys.* **2002**, *116*, 561–570.

(39) Fritsky, I. O.; Swiatek-Kozłowska, J.; Kapshuk, A. A.; Kozłowski, H.; Sliva, T. Yu.; Gumienna-Kontecka, E.; Prisyazhnaya, E. V.; Iskenderov, T. S. *Z. Naturforsch., Teil B* **2000**, *55*, 966–970.

Table 2. Comparison of Hydrogen Bond Structural Parameters for (H₂O)NO₃⁻ Complexes **1** and **2**^a

parameter	complex 1				complex 2				X-ray ^b
	BP86/ DN**	B3LYP/ TZVP	B3LYP/ TZVP+	MP2/aug- cc-pVDZ	BP86/ DN**	B3LYP/ TZVP	B3LYP/ TZVP+	MP2/aug- cc-pVDZ	
strong O···H(O) hydrogen bond									
<i>d</i>	1.86	1.86	1.88	1.86	1.85	1.79	1.81	1.83	1.89 ± 0.07
O···H–O angle	152	162	161	163	153	160	158	160	163 ± 9
N–O···H angle	112	109	109	108	114	119	123	113	116 ± 14
O ₁ –N–O···H dihedral	0	0	0	0	0	0	0	0	0 ± 30
O ₂ –N–O···H dihedral	180	180	180	180	180	180	180	180	180 ± 30
weak O···H(O) hydrogen bond									
<i>d</i>	2.34	2.36	2.39	2.35					
O···H–O angle	123	122	122	123					
N–O···H angle	109	109	109	110					
O ₁ –N–O···H dihedral	0	0	0	0					
O ₂ –N–O···H dihedral	180	180	180	180					

^a Units: distances in angstroms, angles in degrees. ^b Uncertainties in X-ray values represent one standard deviation from the mean observed for 150 fragments in which 1.5 ≤ *d* ≤ 2.0 Å.

Table 3. Comparison of Hydrogen Bond Structural Parameters for (MeOH)NO₃⁻ Complexes **3** and **4**^a

parameter	complex 3				complex 4				X-ray ^b
	BP86/ DN**	B3LYP/ TZVP	B3LYP/ TZVP+	MP2/aug- cc-pVDZ	BP86/ DN**	B3LYP/ TZVP	B3LYP/ TZVP+	MP2/aug- cc-pVDZ	
strong O···H(O) hydrogen bond									
<i>d</i>	1.73	1.75	1.78	1.77	1.72	1.76	1.79	1.83	1.85 ± 0.09
O···H–O angle	171	176	176	173	163	162	161	154	161 ± 8
N–O···H angle	113	116	117	110	118	118	120	108	114 ± 12
O ₁ –N–O···H dihedral	0	4	4	2	0	0	0	0	0 ± 21
O ₂ –N–O···H dihedral	180	176	177	178	180	180	180	180	180 ± 21
weak O···H(C) hydrogen bond ^c									
<i>d</i>	2.98	2.65	2.65	2.86	2.78 ± 0.17				
O···H–C angle	94	125	127	93	116 ± 10				
N–O···H angle	117	118	117	120	114 ± 13				
O ₁ –N–O···H dihedral	19	12	11	22	18 ± 31				
O ₂ –N–O···H dihedral	161	168	169	158	163 ± 31				

^a Units: distances in angstroms, angles in degrees. ^b Uncertainties in the X-ray values represent one standard deviation from the mean observed for 38 fragments in which 1.5 ≤ *d* ≤ 2.0 Å. ^c Experimental data for the weak O···H(C) bond was taken from 7 fragments in which the O···H(C–OH) distance was between 2.0 and 3.0 Å.

Table 4. Comparison of Hydrogen Bond Structural Parameters for (NMF)NO₃⁻ Complex **5**^a

parameter	BP86/ DN**	B3LYP/ TZVP	B3LYP/ TZVP+	MP2/aug- cc-pVDZ	X-ray ^b
strong O···H(N) hydrogen bond					
<i>d</i>	1.76	1.80	1.82	1.81	1.91 ± 0.06
O···H–N angle	174	175	177	172	167 ± 7
N–O···H angle	109	109	110	103	118 ± 16
O ₁ –N–O···H dihedral	0	0	0	0	0 ± 27
O ₂ –N–O···H dihedral	180	180	180	180	180 ± 27
weak O···H(C) hydrogen bond					
<i>d</i>	2.52	2.52	2.54	2.46	
O···H–C angle	133	133	134	129	
N–O···H angle	127	128	127	134	
O ₁ –N–O···H dihedral	0	0	0	0	
O ₂ –N–O···H dihedral	180	180	180	180	

^a Units: distances in angstroms, angles in degrees. ^b Uncertainties in X-ray values represent one standard deviation from the mean observed for 36 fragments in which 1.5 ≤ *d* ≤ 2.0 Å.

amide is within 2.0 Å of a NO₃⁻ oxygen atom. Again the experimental structures for RC(=O)RNH–ONO₂⁻ exhibit structural features similar to those observed in **5**.

Finally, there are numerous examples in the CSD, 735 cases, in which an aliphatic C–H donor group is within 2.5 Å of a NO₃⁻ oxygen atom. The geometric parameters for the C–H···O hydrogen bonds show more scatter than those involving O–H and N–H donor groups. Although the data do suggest a

Table 5. Comparison of Hydrogen Bond Structural Parameters for (CH₄)NO₃⁻ Complex **6**^a

parameter	complex 6				X-ray ^b
	BP86/ DN**	B3LYP/ TZVP	B3LYP/ TZVP+	MP2/aug- cc-pVDZ	
O···H distance, <i>d</i>	2.26	2.40	2.43	2.43	2.39 ± 0.09
O···H–C angle	176	164	170	163	147 ± 16
N–O···H angle	117	105	116	98	123 ± 23
O ₁ –N–O···H dihedral	4	0	0	0	nd ^c
O ₂ –N–O···H dihedral	176	180	180	180	nd ^c

^a Units: distances in angstroms, angles in degrees. ^b Uncertainties in X-ray values represent one standard deviation from the mean observed for 786 fragments in which 1.5 ≤ *d* ≤ 2.5 Å. ^c There was no discernible preference for the O–N–O···H dihedral angles.

preference for a linear C–H···O angle and a bent N–O···H angle, there is no discernible O–N–O···H orientation. This behavior is consistent with the fact that C–H donor groups form bonds that are significantly weaker than O–H and N–H donor groups (vide infra), and therefore, C–H···O interactions are more easily distorted from their optimal geometries.¹⁵

Electronic Binding Energies. Electronic binding energies, Δ*E*, for **1–6** at various levels of theory are presented in Table 6. The MP2/CBS numbers are the most accurate Δ*E* values reported in this study. Comparison of these values to those obtained at the other MP2 levels of theory provides an estimate of the magnitude of the basis set superposition error, BSSE,

Table 6. Electronic Binding Energies (ΔE) in kcal/mol for NO_3^- Complexes **1–6** at Various Levels of Theory^a

complex	BP86/ DN**	B3LYP/ TZVP	B3LYP/ TZVP+	MP2/aug- cc-pVDZ	MP2/aug- cc-pVTZ	MP2/aug- cc-pVQZ	MP2/ CBS
1	-15.04	-16.82	-15.59	-16.09	-16.03	-15.94	-15.88
2	-12.99	-14.21	-13.09	-13.44	-13.36	-13.23	-13.15
3	-14.54	-15.75	-14.24	-16.21	-15.98	-15.74	-15.59
4	-13.46	-14.56	-13.18	-14.93	-14.74	-14.52	-14.37
5	-20.84	-22.17	-23.76	-23.75	-23.22	-22.79	-22.71
6	-1.71	-2.59	-1.83	-3.43	-3.10	-2.91	-2.78

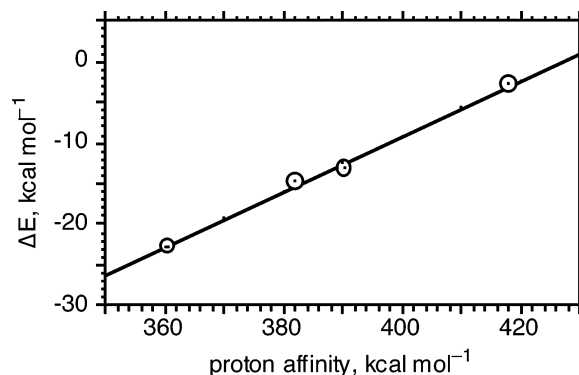
$$^a \Delta E = E_{\text{elec}}(\text{complex}) - E_{\text{elec}}(\text{NO}_3^-) - E_{\text{elec}}(\text{D-H}).$$

present when using this series of correlation-consistent basis sets. With the smallest basis set, aug-cc-pVDZ, the differences range from 0.21 to 1.0 kcal/mol. As expected, there is a correlation between the size of the complex and the magnitude of the BSSE, which increases in the order $\text{H}_2\text{O} < \text{CH}_4 \sim \text{MeOH} < \text{NMF}$ (when there are more basis functions on the donor, the BSSE is larger). The MP2/CBS ΔE values also provide a benchmark against which the accuracy of the three levels of DFT can be compared. The BP86/DN** level, which may not have the required diffuse character in the DN numerical basis set, systematically underestimates the ΔE values with an average discrepancy of 1.28 kcal/mol. The MP2/CBS values are better reproduced by using the larger basis sets with the B3LYP functional. There is an average absolute accuracy of 0.57 kcal/mol at the B3LYP/TZVP level and 0.75 kcal/mol at the B3LYP/TZVP+ level.

The MP2/CBS ΔE values of -15.9 and -13.2 kcal/mol for **1** and **2**, respectively, are consistent with prior theoretical studies on $(\text{H}_2\text{O})\text{NO}_3^-$ complexes. Hartree–Fock calculations, which give a C_{2v} symmetry minimum for the bidentate form, yielded ΔE values of -18.5 and -17.2 kcal/mol, respectively, with a 6-31G basis set³⁴ and -14.9 and -12.3 kcal/mol, respectively, with a polarized double- ζ basis set.³⁵ ΔE values at the B3LYP/aug-cc-pVTZ level are -14.5 kcal/mol for **1** and -12.6 kcal/mol for **2**,^{37,38} as compared to our B3LYP values of -16.8 and -14.9 kcal/mol with the TZVP basis set and -15.6 and -13.1 kcal/mol with the TZVP+ basis set.

The ΔE values for O–H and N–H donor groups, **1–5**, are in the range of -13 to -23 kcal/mol, which classifies these as examples of “strong” (> 10 kcal/mol) hydrogen bonds.¹⁴ For comparison hydrogen bonds, formed between neutral donor and acceptor groups, typically exhibit ΔE values within the range of 3 to 10 kcal/mol. In addition, NO_3^- forms a C–H \cdots O hydrogen bonded complex with CH_4 , **6**, having $\Delta E = -2.78$ kcal/mol. This value is significantly stronger than CH_4 hydrogen bonds in complexes with neutral oxygen acceptors, for example, H_2O , formaldehyde, and acetamide, where calculated ΔE values range from -0.3 to -0.8 kcal/mol.⁴⁰ The presence of a C–H \cdots O interaction in **3** accounts for the increased stability when compared to **4**. In addition, **5** is stabilized by a C–H \cdots N interaction with the N– CH_3 group.

In a prior study of C–H \cdots O interactions,^{31a} we observed that calculated ΔE values for a series of different hydrogen bond donors were correlated linearly with experimental gas-phase proton affinities for their conjugate anions where the proton

**Figure 6.** Plot of ΔE versus the proton affinity for the conjugate anion, D^- , of the donor group D–H.

affinity of the anion is defined as the enthalpy associated with the reaction $\text{AH} \rightarrow \text{A}^- + \text{H}^+$. Donor groups with higher acidity form stronger hydrogen bond complexes. A similar correlation holds for the NO_3^- complexes examined in this study. When the ΔE values for complexes **2**, **4**, **5**, and **6**, are plotted against the proton affinities for OH^- , MeO^- , HC(=O)NCH_3^- , and CH_3^- ,⁴¹ the linear correlation shown in Figure 6 is obtained.

Potential Energy Surfaces for Selected Structural Distortions in 4 and 5. Potential energy surfaces for distortions of d , D–H \cdots O angle, N–O \cdots H angle, and O–N–O \cdots H dihedral angle (D = O or N) provide further insight by showing the extent of destabilization to the D–H \cdots ONO $_2^-$ hydrogen bond that would result from variation in the geometric parameters. We performed a series of calculations to generate these PES's for distortions of structural parameters of the O–H hydrogen bond in **4** and the N–H hydrogen bond in **5**.

Plots of relative energy (B3LYP/TZVP+) versus structural distortions of **4** are presented in Figure 7. The Y-axes are identical in each case to allow for a direct visual comparison of the different plots. A useful point of comparison between the potential energy surfaces is the extent of distortion required to give a 1.0 kcal/mol decrease in binding energy for the complex. Examination of each plot yields the following results for **4** (low 1 kcal/mol threshold \leq minimum \leq high 1 kcal/mol threshold): d , $1.60 \leq 1.79 \leq 2.06$ Å; O–H \cdots O angle, $144 \leq 161 \leq 180^\circ$; N–O \cdots H angle, $101 \leq 120 \leq 148^\circ$; O–N–O \cdots H dihedral angle, $-53 \leq 0 \leq 53^\circ$ or $127 \leq 180 \leq 233^\circ$. Thus, the variation in d is ~ 0.2 Å, the variation in the O–H \cdots O angle is $\sim 20^\circ$, the variation in the N–O \cdots H angle is $\sim 20^\circ$, and the variation in O–N–O \cdots H dihedral angle is $\sim 50^\circ$. The analogous plots for **5** (not shown, see Supporting Information) are similar to those of **4** yielding the following results: variation in d , ~ 0.2 Å; variation in the N–H \cdots O angle, $\sim 20^\circ$, variation in N–O \cdots H angle, $\sim 15^\circ$; variation in O–N–O \cdots H dihedral angle, $\sim 30^\circ$.

Histograms of the distributions of geometric parameters observed in the X-ray data are shown above each potential energy surface in Figure 7. In all cases, the bulk of the data lies within 1.0 kcal/mol from the minima. This result is consistent with the computations and further validates the

(40) (a) Rovira, M. C.; Novoa, J. J.; Whangbo, M.-H.; Williams, J. M. *Chem. Phys.* **1995**, *200*, 319–335. (b) Gu, Y.; Kar, T.; Scheiner, S. *J. Am. Chem. Soc.* **1999**, *121*, 9411–9422. (c) Novoa, J. J.; Mota, F. *Chem. Phys. Lett.* **1997**, *266*, 23–30. (d) Kim, K. S.; Friesner, R. A. *J. Am. Chem. Soc.* **1997**, *119*, 12 952–12 961.

(41) Experimental gas-phase proton affinities (kcal mol $^{-1}$): (a) OH^- , 390.3 ± 0.3 , Schulz, P. A.; Mead, R. D.; Jones, P. L.; Lineberger, W. C. *J. Chem. Phys.* **1982**, *77*, 1153–1165. (b) MeO^- , 382 ± 1 , Ramond, T. M.; Davico, G. E.; Schwartz, R. L.; Lineberger, W. C. *J. Chem. Phys.* **2000**, *112*, 1158–1169. (c) $\text{HC(=O)N(CH}_3^-)$, 360.4 ± 2.1 , Taft, R. W. *Prog. Phys. Org. Chem.* **1987**, *16*, 1. (d) CH_3^- , 418.0 ± 3.5 , Graul, S. T.; Squires, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2517–2529.

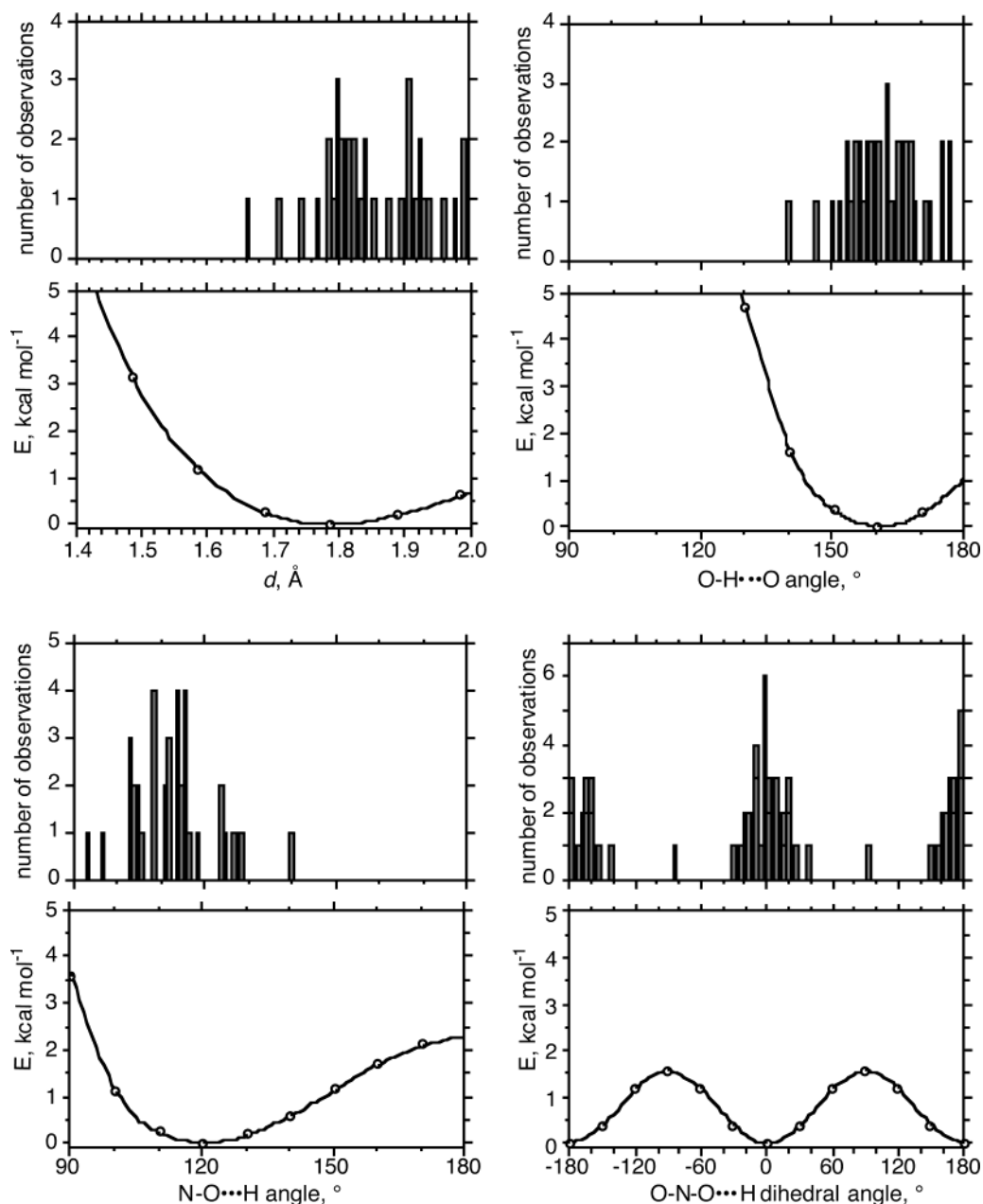


Figure 7. Comparison of experimental distributions of geometric parameters with potential energy surfaces (PES) obtained at the B3LYP/TZVP+ level of theory for the $(\text{MeOH})\text{NO}_3^-$ complex, **4**: d (top left), $\text{O}-\text{H}\cdots\text{O}$ angle (top right), $\text{N}-\text{O}\cdots\text{H}$ angle (bottom left), $\text{O}-\text{N}-\text{O}\cdots\text{H}$ dihedral angle (bottom right).

comparison of “gas-phase” calculations to condensed-phase results. The agreement confirms that the hydrogen bonding geometries observed in the crystal structures are the result of intrinsic geometric preferences that are also captured by the electronic structure (DFT or MP2) calculations on isolated one-to-one complexes.

Coordination Number and Host Cavity Radius. The electrostatic potential surface (Figure 4) reveals that NO_3^- has an intrinsic hydrogen bonding topography in which there are six equivalent positions representing energy minima for placing positive charge about the anion. This result suggests that the ideal NO_3^- host would provide six D–H groups, constrained in space to converge at the binding sites on the anion (Figure 8a). However, the general analysis of NO_3^- hydrogen bonding in crystal structures, which intentionally focused on nonchelating D–H groups, yielded an average number of only two to three short contacts per anion (vide supra), revealing that only half

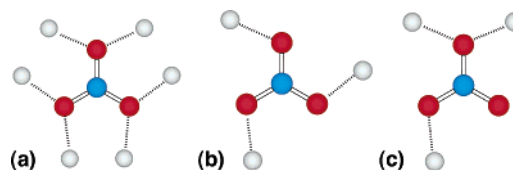


Figure 8. Strongest hydrogen bonds are formed with NO_3^- when H atoms are located in one of six positions (a). For monoprotic D–H groups, there are two motifs for placing three H atoms about NO_3^- , one using all three oxygen atoms (b) and one using only two oxygen atoms (c).

of the six sites are typically occupied. An explanation for this behavior is provided by a consideration of steric factors. At an $\text{H}\cdots\text{O}$ contact distance of 1.90 Å, two protons sharing an edge of the triangle defined by the NO_3^- oxygen atoms are 1.86 Å apart. This close contact would result in large repulsive Coulombic and van der Waals interactions.⁴² Thus, there is sufficient space to place only one D–H group on each of the

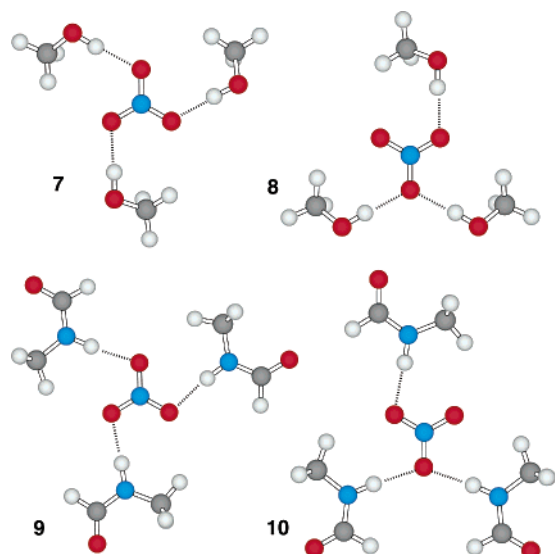


Figure 9. B3LYP/TZVP optimized geometries for (MeOH)₃NO₃⁻ complexes, **7** and **8**, and (NMF)₃NO₃⁻ complexes, **9** and **10**.

three edges of the triangle defined by the NO₃⁻ oxygen atoms. The D–H groups can be distributed in one of two motifs. In the symmetrical motif, there is a hydrogen bond to each oxygen atom (Figure 8b). In the asymmetric motif, one oxygen atom has two hydrogen bonds, one has one hydrogen bond, and one has no hydrogen bonds (Figure 8c).

To evaluate optimal cavity sizes for receptors constructed by connecting three mono-protic D–H groups, geometries for both motifs were obtained for (MeOH)₃NO₃⁻ and (NMF)₃NO₃⁻ complexes at the B3LYP/TZVP level of theory. The optimized geometries, shown in Figure 9, exhibit the following *d* values: **7**, 1.86 Å, **8**, 1.86 Å, **9**, 1.93 Å, **10**, 1.94 Å. The contact distances yield cavity radii, defined as the distance from the center of the cavity to the D–H hydrogen atoms of 2.68, 2.68, 2.64, and 2.64 Å, respectively. It should be noted that the D–H vectors do not converge at the center of the cavity, but rather at the oxygen acceptor atoms of the anion. In both cases, the two motifs were essentially the same in energy, with electronic binding energies, Δ*E* (see Table 6 for comparison with values for one-to-one complexes), of –40.31 and –39.99 kcal/mol for **7** and **8**, respectively, and –53.98 and –53.82 for **9** and **10**, respectively.

Further examination of the CSD reveals that these two binding motifs are fairly common in the solid state. Figure 10 shows three examples of the symmetric motif, **11–13**,^{43–45} and three examples of the asymmetric motif, **14–15**,^{46–48} which show very similar structural features to those calculated for **7–10**. In these experimental examples, *d* ranges from 1.80 to 1.95 Å and cavity radii range from 2.53 to 2.79 Å, corroborating the

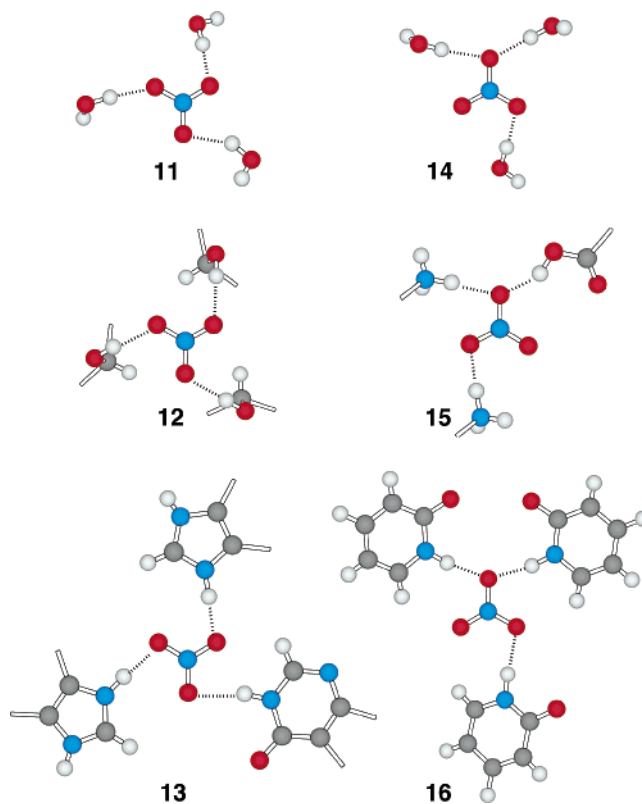


Figure 10. Examples of hydrogen bonding motifs (see Figure 8b,c) found in the CSD. In the crystal structure examples shown here, only partial structures are shown for clarity. The three oxygen motif is found in **11**,⁴³ **12**,⁴⁴ and **13**.⁴⁵ The two oxygen motif is found in **14**,⁴⁶ **15**,⁴⁷ and **16**.⁴⁸

calculated geometries and defining a fairly narrow range for the cavity size of a tridentate host architecture.

Summary

This study has identified the existence of a clear set of structural criteria for the rational design of molecular receptors that complex the NO₃⁻ anion through hydrogen bonding interactions. Such criteria make it possible to define input geometries for software such as CAVEAT⁴⁹ and HostDesigner,⁵⁰ which are computer-aided-design programs that apply de novo design strategies to construct receptors around guest species. In addition, the definition of “convergent” binding sites provides the structural basis needed to evaluate the degree of D–H organization that is offered by both new and existing host architectures.

The results show that NO₃⁻ has an intrinsic hydrogen bonding topography in which there are six optimal sites for proton location. The geometric features observed in crystal structures and in the optimized geometries of complexes **1–10** are explained by a preference to locate the D–H protons in these positions. This preference characterizes convergent hydrogen bonding in NO₃⁻ anion receptors. For the strongest hydrogen bonding interaction, the N–O···H angle will be bent at an angle of 115 ± 10°, and the hydrogen atom will lie in the NO₃⁻ plane giving O–N–O···H dihedral angles of 0° and 180°. In addition, the D–H vector will point toward the oxygen atom, giving

(42) (a) When two isolated alcohol protons with partial atomic charges of +0.2 are separated by 1.86 Å, MM3^{2b} calculations yield a repulsive interaction energy of 16.8 kcal/mol. (b) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551–8566.

(43) Prins, R.; de Graaff, R. A. G.; Haasnoot, J. G.; Vader, C.; Reedijk, J. *J. Chem. Soc. Chem. Commun.* **1986**, 1430–1431.

(44) Smith, G. T.; Mallinson, P. R.; Frampton, C. S.; Farrugia, L. J.; Peacock, R. D.; Howard, J. A. K. *J. Am. Chem. Soc.* **1997**, *119*, 5028–5034.

(45) Rosenstein, R. D.; Oberding, M.; Hyde, J. R.; Zubieta, J.; Karlin, K. D.; Seeman, N. C. *Cryst. Struct. Commun.* **1982**, *11*, 1507–1513.

(46) Ahrens, B.; Cotton, S. A.; Feeder, N.; Noy, O. E.; Raithby, P. R.; Teat, S. J. *J. Chem. Soc., Dalton Trans.* **2002**, 2027–2030.

(47) Mostad, A.; Natarajan, S. Z. *Kristallogr.* **1985**, *172*, 175–182.

(48) Goodgame, D. M. L.; Newnham, S.; O'Mahoney, C. A.; Williams, D. J. *Polyhedron* **1990**, *9*, 491–494.

(49) Lauri, G.; Bartlett, P. A. *J. Comput. Aided. Mol. Design* **1994**, *8*, 51–66.

(50) (a) Hay, B. P.; Firman, T. K. *Inorg. Chem.* **2002**, *41*, 5502–5512. (b) Hay, B. P.; Firman, T. K. *HostDesigner User's Manual*; Pacific Northwest National Laboratory: Richland, Washington, 2003, <http://hostdesigner.emsl.pnl.gov>.

D–H···O angles that are near linear, $170 \pm 10^\circ$. Potential energy surfaces show that while there is some flexibility, distortions from this convergent geometry can result in significant loss of interaction energy. For example, a RO–H group constrained to give a linear N–O···H angle would weaken the interaction by 2.3 kcal/mol, a 17% loss of the hydrogen bond energy in **4**.

An important observation that emerges from this study is that although the NO_3^- anion should be able to accommodate six strong D–H groups, steric crowding may make it difficult to identify scaffolds that can converge more than three simple D–H groups about the anion. A possible solution to this problem is to use diprotic donor groups, such as urea or guanidinium, which are able to contact the two adjacent binding sites on one edge of the oxyanion. Such diprotic groups have long been incorporated into anion receptor designs.⁵¹ Recent theoretical results suggest that it is possible to chelate three nonconnected urea groups to NO_3^- ,⁵² achieving the desired coordinative saturation without adverse steric effects.

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Supporting Information Available: Cartesian coordinates for the MP2/aug-cc-pVDZ optimized structures **1–6** and B3LYP/TZVP optimized structures **7–10**, and potential energy surfaces for selected distortions of **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(51) (a) Dietrich, B.; Fyles, T. M.; Lehn, J. M.; Pease, L. G.; Fyles, D. L. *J. Chem. Soc. Chem. Commun.* **1978**, 934–936. (b) Dietrich, B.; Fyles, D. L.; Fyles, T. M.; Lehn, J. M. *Helv. Chim. Acta* **1979**, *62*, 2763–2787.

(52) Herges, R.; Dikmaus, A.; Jana, U.; Köhler, F.; Jones, P. G.; Dix, I.; Fricke, T.; König, B. *Eur. J. Org. Chem.* **2002**, 3004–3014.