

$^3\text{h}J(^{15}\text{N}-^{31}\text{P})$ Spin-Spin Coupling Constants across N-H \cdots O-P Hydrogen BondsJanet E. Del Bene,^{*,†,‡} S. Ajith Perera,[‡] Rodney J. Bartlett,[‡] José Elguero,[§] Ibon Alkorta,[§] Carmen López-Leonardo,^{||} and Mateo Alajarin^{||}*Contribution from the Department of Chemistry, Youngstown State University, Youngstown, Ohio 44555, Quantum Theory Project, University of Florida, Gainesville, Florida 32611, Instituto de Química Médica, CSIC, Juan de la Cierva, 3, E-28006 Madrid, Spain, and Departamento de Química Orgánica, Facultad de Química, Universidad de Murcia, Campus de Espinardo, E-30100 Murcia, Spain*

Received July 19, 2001. Revised Manuscript Received February 19, 2002

Abstract: Equation-of-motion coupled cluster singles and doubles (EOM-CCSD) calculations have been performed to evaluate three-bond $^{15}\text{N}-^{31}\text{P}$ coupling constants ($^3\text{h}J_{\text{N-P}}$) across N-H \cdots O-P hydrogen bonds in model cationic and anionic complexes including $\text{NH}_4^+:\text{OPH}$, $\text{NH}_4^+:\text{OPH}_3$, $\text{NH}_3^+:\text{O}_2\text{PH}_2$, $\text{NFH}_2^+:\text{O}_2\text{PH}_2$, and $\text{NF}_2\text{H}^+:\text{O}_2\text{PH}_2$. Three-bond coupling constants can be appreciable when the phosphorus is P(V), but are negligible with P(III). $^3\text{h}J_{\text{N-P}}$ values in complexes with cyclic or open structures are less than 1 Hz, a consequence of the nonlinear arrangement of N, H, O, and P atoms. For complexes with these structures, $^3\text{h}J_{\text{N-P}}$ may not be experimentally measurable. In contrast, complexes in which the N, H, O, and P atoms are collinear or nearly collinear have larger values of $^3\text{h}J_{\text{N-P}}$, even though the N-P distances are longer than N-P distances in cyclic and open structures. In linear complexes, $^3\text{h}J_{\text{N-P}}$ is dominated by the Fermi-contact term, which is distance dependent. Therefore, N-P (and hydrogen-bonding N-O) distances in these complexes can be determined from experimentally measured $^{15}\text{N}-^{31}\text{P}$ coupling constants.

Introduction

The observation of two-bond NMR X-Y spin-spin coupling constants ($^2\text{h}J_{\text{X-Y}}$) across X-H-Y hydrogen bonds has led to a great deal of excitement and activity in the chemical, biochemical, and theoretical chemistry communities.¹⁻¹⁴ Very recently, Shirakawa et al.¹⁵ reported a study of three-bond

$^{15}\text{N}-^{31}\text{P}$ spin-spin coupling constants ($^3\text{h}J_{\text{N-P}}$) across N-H \cdots O-P hydrogen bonds in protein:nucleotide complexes. The observation of such couplings is interesting in itself, and may have important consequences, given the crucial role that hydrogen bonds play in the three-dimensional structures of these complexes, and hence in their reactivity. However, what is perhaps even more intriguing is the observation that among the five complexes examined, only one yielded an appreciable coupling constant. The authors speculated as to why this might be so. They stated, "It is possible that the linear arrangement of the ^{31}P nucleus relative to hydrogen and H-bond accepting oxygen nuclei is a prerequisite for the presence of observable trans-H-bond couplings."

We have previously reported data showing the dependence of $^2\text{h}J_{\text{N-N}}$ on the linearity of the hydrogen bond and the orientation of the proton-acceptor molecule.¹⁴ To further establish these relationships, we will investigate $^3\text{h}J_{\text{N-P}}$ coupling constants in several model systems with N-H \cdots O-P hydrogen bonds, and examine the geometry dependence of $^3\text{h}J_{\text{N-P}}$. We have already demonstrated that NMR spin-spin coupling constants across hydrogen bonds computed using equation-of-motion coupled cluster singles and doubles (EOM-CCSD) theory are reliable, and have predictive value.^{5,7,10,11,16} The present study provides an excellent example of the unique role that such a theory can play in supporting and understanding experimental studies, since it is possible for us to arrange the hydrogen-bonded

* To whom correspondence should be addressed. E-mail: fr042008@ysub.yosu.edu.

† Youngstown State University.

‡ University of Florida.

§ Instituto de Química Médica.

|| Universidad de Murcia.

- (1) Shenderovich, I. G.; Smirnov, S. N.; Denisov, G. S.; Gindin, V. A.; Golubev, N. S.; Dunger, A.; Reibke, R.; Kirpekar, S.; Malkina, O. L.; Limbach, H.-H. *Ber. Bunsen-Ges. Phys. Chem.* **1998**, *102*, 422.
- (2) Dingley, A. G.; Grzesiek, S. *J. Am. Chem. Soc.* **1998**, *120*, 8293.
- (3) Dingley, A. J.; Masse, J. E.; Peterson, R. D.; Barfield, M.; Feigon, J.; Grzesiek, S. *J. Am. Chem. Soc.* **1999**, *121*, 6019.
- (4) Scheurer, C.; Brüschweiler, R. *J. Am. Chem. Soc.* **1999**, *121*, 8661.
- (5) Perera, S. A.; Bartlett, R. J. *J. Am. Chem. Soc.* **2000**, *122*, 1231.
- (6) Del Bene, J. E.; Perera, S. A.; Bartlett, R. J. *J. Am. Chem. Soc.* **2000**, *122*, 3560.
- (7) Del Bene, J. E.; Jordan, M. J. T. *J. Am. Chem. Soc.* **2000**, *122*, 4794.
- (8) Benedict, H.; Shenderovich, I. G.; Malkina, O. L.; Malkin, V. G.; Denisov, G. S.; Golubev, N. S.; Limbach, H.-H. *J. Am. Chem. Soc.* **2000**, *122*, 1979.
- (9) Pecul, M.; Leszczynski, J.; Sadlej, J. *J. Phys. Chem. A* **2000**, *104*, 8105; *J. Chem. Phys.* **2000**, *112*, 7930.
- (10) Del Bene, J. E.; Bartlett, R. J. *J. Am. Chem. Soc.* **2000**, *122*, 10480.
- (11) Del Bene, J. E.; Perera, S. A.; Bartlett, R. J. *J. Phys. Chem. A* **2001**, *105*, 930.
- (12) Barfield, M.; Dingley, A. J.; Feigon, J.; Grzesiek, S. *J. Am. Chem. Soc.* **2001**, *123*, 4014.
- (13) Chapman, K.; Crittenden, D.; Bevitt, J.; Jordan, M. J. T.; Del Bene, J. E. *J. Phys. Chem. A* **2001**, *105*, 5442.
- (14) Del Bene, J. E.; Perera, S. A.; Bartlett, R. J. *J. Magn. Reson.* **2001**, *39*, S109.
- (15) Mishima, M.; Hatanaka, M.; Yokoyama, S.; Ikegami, T.; Wälchli, M.; Ito, Y.; Shirakawa, M. *J. Am. Chem. Soc.* **2000**, *122*, 5883.

- (16) Del Bene, J. E.; Perera, S. A.; Bartlett, R. J.; Alkorta, I.; Elguero, J. *J. Phys. Chem. A* **2000**, *104*, 7165.

molecules in different conformations and then compute the coupling constant for each arrangement. We can then answer the question of which orientation gives the largest coupling constant.

Method of Calculation

The models used for this study include both cationic and anionic complexes having $N-H\cdots O-P$ and $N-H\cdots O-P$ hydrogen bonds, respectively. The cationic complexes are $NH_4^+ : OPH$ and $NH_4^+ : OPH_3$, and the anionic complexes include $NH_3^- : O_2PH_2$, $NFH_2^- : O_2PH_2$, and $NF_2H^- : O_2PH_2$. The cyclic, open, and linear structures of selected complexes considered are optimized structures at second-order perturbation theory [MBPT(2) = MP2]^{17–20} with the 6-31+G(d,p) basis set.^{21–25}

NMR spin–spin coupling constants are obtained from equation-of-motion coupled cluster singles and doubles (EOM-CCSD) theory in the CI-like approximation.^{26–29} For these calculations, a qzvp basis set was used on N and O, qz2p on P and the hydrogen-bonded proton,³⁰ and Dunning's cc-pVDZ basis^{31,32} on other hydrogens. The Ahlrichs basis set³⁰ has been found useful for the calculation of NMR parameters. The coupling constant calculations are done with the ACES II program.³³ All calculations were carried out on the Cray T94 and SV1 computers at the Ohio Supercomputer Center.

Results and Discussion

Structures of Complexes. The optimized structure of the complex $NH_4^+ : OPH$ [with P(III)] has C_s symmetry, with an N–O distance of 2.694 Å, a slightly nonlinear N–H \cdots O hydrogen bond, and an N–O–P angle of 158°. A second complex was also optimized with N, H, O, and P atoms constrained to be collinear. This “linear” complex has a slightly greater N–O distance of 2.704 Å, but is only 0.4 kcal/mol less stable than the fully optimized structure. The fully optimized structure of the complex $NH_4^+ : OPH_3$ [with P(V)] also has C_s symmetry, with an N–O distance of 2.582 Å, a slightly

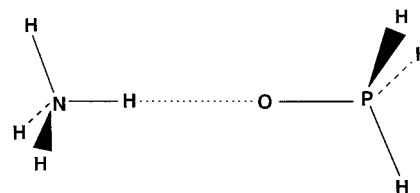


Figure 1. The optimized linear structure of $NH_4^+ : OPH_3$.

Table 1. Selected Structural Parameters and Electronic Binding Energies (ΔE_b) for Complexes $NH_4^+ : OPH$ and $NH_4^+ : OPH_3^a$

	sym	N–O	N–H	$\angle H-N-O$	$\angle N-O-P$	ΔE_b
$NH_4^+ : OPH$						
optimized	C_s	2.694	1.052	4	158	–23.0
opt. linear	C_s	2.704	1.049	0 ^b	180 ^b	–22.6
$NH_4^+ : OPH_3^c$						
optimized	C_s	2.582	1.070	4	167	–33.7
opt. linear	C_{3v}	2.588	1.067	0 ^b	180 ^b	–33.6

^a Distances in Å; angles in deg; energies in kcal/mol. ^b In the linear structures, these angles were constrained during the structure optimization. ^c The NH_3 and PH_3 groups are staggered.

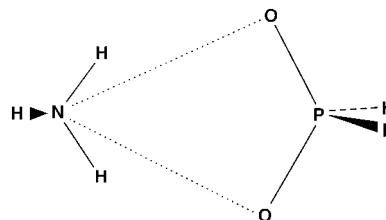


Figure 2. The equilibrium cyclic structure of $NH_3^- : O_2PH_2$.

nonlinear N–H \cdots O hydrogen bond, and an N–O–P angle of 167°. An optimized “linear” structure of C_{3v} symmetry was found to have an N–O distance of 2.588 Å. This structure, which is shown in Figure 1, is only 0.1 kcal/mol less stable than the fully optimized structure. Selected structural parameters and binding energies for these complexes are reported in Table 1.

For $NH_3^- : O_2PH_2$, a cyclic structure stabilized by two distorted N–H \cdots O hydrogen bonds, four open structures stabilized by a single hydrogen bond, and a linear structure were obtained. The global minimum on the potential surface is the cyclic structure of C_s symmetry, shown in Figure 2. Among the optimized structures for $NH_3^- : O_2PH_2$, the cyclic structure has the longest N–O distance of 3.172 Å, but the shortest N–P distance of 3.611 Å. Four open structures of C_s symmetry in which only one N–H \cdots O hydrogen bond can form were also optimized. These isomers have the O–P bond (hydrogen-bonded O) cis or trans to the NH_2 group with respect to the hydrogen-bonding N–O line. For each isomer, the PH_2 group may be either cis or trans to the hydrogen-bonded N–H with respect to the O–P (hydrogen-bonded O) bond. None of the open isomers are equilibrium structures on the potential surface. The most stable open isomer has the O–P bond (hydrogen-bonded O) cis to the NH_2 group, and the PH_2 group trans to N–H, as shown in Figure 3. This complex is stabilized by a slightly nonlinear hydrogen bond and has an N–O–P angle of 126°. The N–O and N–P distances are 3.001 and 4.087 Å, respectively. This open structure is only 0.4 kcal/mol less stable than the equilibrium cyclic structure. Another open structure was found in which the N, H, O, and P atoms were constrained to be collinear. This complex, shown in Figure 4, has the shortest

- (17) Bartlett, R. J.; Silver, D. M. *J. Chem. Phys.* **1975**, *62*, 3258.
 (18) Bartlett, R. J.; Purvis, G. D. *Int. J. Quantum Chem.* **1978**, *14*, 561.
 (19) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem., Quantum Chem. Symp.* **1976**, *10*, 1.
 (20) Krishnan, R.; Pople, J. A. *Int. J. Quantum Chem.* **1978**, *14*, 91.
 (21) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.
 (22) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.
 (23) Spitznagel, G. W.; Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comput. Chem.* **1982**, *3*, 363.
 (24) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.
 (25) Structure optimizations were done with Gaussian 98. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.
 (26) Perera, S. A.; Sekino, H.; Bartlett, R. J. *J. Chem. Phys.* **1994**, *101*, 2186.
 (27) Perera, S. A.; Nooijen, M.; Bartlett, R. J. *J. Chem. Phys.* **1996**, *104*, 3290.
 (28) Perera, S. A.; Bartlett, R. J. *J. Am. Chem. Soc.* **1995**, *117*, 8476.
 (29) Perera, S. A.; Bartlett, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 7849.
 (30) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.
 (31) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.
 (32) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1995**, *103*, 4572.
 (33) ACES II is a program product of the Quantum Theory Project, University of Florida. Authors: Stanton, J. F.; Gauss, J.; Watts, J. D.; Nooijen, M.; Oliphant, N.; Perera, S. A.; Szalay, P. G.; Lauderdale, W. J.; Gwaltney, S. R.; Beck, S.; Balkova, A.; Bernholdt, D. E.; Baeck, K.-K.; Tozyczko, P.; Sekino, H.; Huber, C.; Bartlett, R. J. Integral packages included are VMOL (Almlöf, J.; Taylor, P. R.); VPROPS (Taylor, P. R.); ABACUS (Helgaker, T.; Jensen, H. J. Aa.; Jorgensen, P.; Olsen, J.; Taylor, P. R.). Brillouin-Wigner perturbation theory was implemented by Pittner, J.

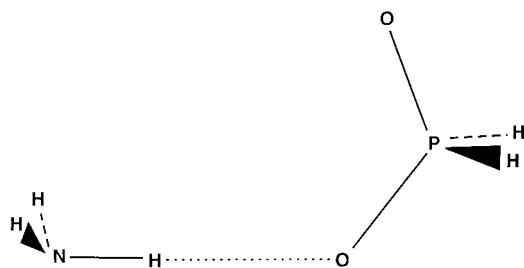


Figure 3. The most stable open isomer of $\text{NH}_3:-\text{O}_2\text{PH}_2$ with a single $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond.

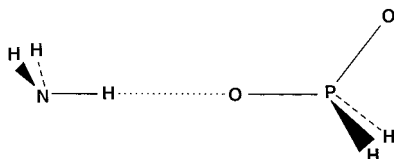


Figure 4. The optimized linear structure of $\text{NH}_3:-\text{O}_2\text{PH}_2$.

Table 2. Selected Structural Parameters and Electronic Binding Energies (ΔE_b) for Complexes $\text{NH}_3:-\text{O}_2\text{PH}_2$, $\text{NFH}_2:-\text{O}_2\text{PH}_2$, and $\text{NF}_2\text{H}:-\text{O}_2\text{PH}_2^a$

	N-O	N-H	N-P	$\angle\text{H}-\text{N}-\text{O}$	$\angle\text{N}-\text{O}-\text{P}$	ΔE_b
$\text{NH}_3:-\text{O}_2\text{PH}_2^b$						
cyclic	3.172	1.019	3.611	26	94	-10.3
open ^c	3.001	1.026	4.087	6	126	-9.9
opt. linear	2.972	1.025	4.502	0 ^d	180 ^d	-9.0
$\text{NFH}_2:-\text{O}_2\text{PH}_2$						
cyclic	3.029	1.026	3.470	24	93	-19.6
$\text{NF}_2\text{H}:-\text{O}_2\text{PH}_2$						
opt. linear	2.675	1.053	4.211	0 ^d	180 ^d	-22.6

^a Distances in Å; angles in deg; energies in kcal/mol. All complexes have C_s symmetry. ^b The cyclic, open, and linear structures are illustrated in Figures 2, 3, and 4, respectively. ^c This structure was constrained to have only one hydrogen bond. ^d In linear structures, these angles were constrained during the structure optimization.

N-O distance of 2.972 Å, and the longest N-P distance of 4.502 Å. The linear complex is 1.3 kcal/mol less stable than the cyclic complex. Selected structural parameters and binding energies for these complexes are reported in Table 2. To increase the strength of the hydrogen bond and decrease the hydrogen bond distance, NFH_2 and NF_2H have also been employed as proton donors to $-\text{O}_2\text{PH}_2$. The global minimum on the $\text{NFH}_2:-\text{O}_2\text{PH}_2$ potential surface is a cyclic C_s structure, which is similar to the cyclic structure on the $\text{NH}_3:-\text{O}_2\text{PH}_2$ surface which is shown in Figure 2. However, it has shorter N-O and N-P distances of 3.029 and 3.470 Å, respectively. The optimized linear complex of $\text{NF}_2\text{H}:-\text{O}_2\text{PH}_2$ is structurally similar to the linear isomer of $\text{NH}_3:-\text{O}_2\text{PH}_2$ shown in Figure 4. Relative to linear $\text{NH}_3:-\text{O}_2\text{PH}_2$, linear $\text{NF}_2\text{H}:-\text{O}_2\text{PH}_2$ has shorter N-O and N-P distances of 2.675 and 4.211 Å, respectively. Selected structural parameters and binding energies for these anionic complexes are also reported in Table 2. All of the complexes investigated in this study are stabilized by traditional $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds.³⁴

NMR Spin-Spin Coupling Constants. There are four terms which contribute to the total spin-spin coupling constant: the paramagnetic spin-orbit (PSO), diamagnetic spin-orbit (DSO), Fermi-contact (FC), and spin dipole (SD). In previous studies, we have demonstrated that two-bond spin-spin coupling constants across $\text{N}-\text{H}-\text{N}$, $\text{N}-\text{H}-\text{O}$, $\text{O}-\text{H}-\text{O}$, and $\text{Cl}-\text{H}-\text{N}$

Table 3. ${}^3\text{h}J_{\text{N}-\text{P}}$ and Components of ${}^3\text{h}J_{\text{N}-\text{P}}$ (Hz) for the Optimized Linear Structures of $\text{NH}_4^+:\text{OPH}$ and $\text{NH}_4^+:\text{OPH}_3$

complex	PSO ^a	DSO ^a	FC ^a	SD ^a	${}^3\text{h}J_{\text{N}-\text{P}}$
$\text{NH}_4^+:\text{OPH}$	-0.2	0.0	0.1	-0.2	-0.3
$\text{NH}_4^+:\text{OPH}_3$	-0.2	0.0	-10.5	-0.2	-10.9

^a PSO = paramagnetic spin-orbit; DSO = diamagnetic spin-orbit; FC = Fermi-contact; SD = spin dipole.

Table 4. ${}^3\text{h}J_{\text{N}-\text{P}}$ (Hz) for Linear $\text{NH}_4^+:\text{OPH}_3$ as a Function of the N-P Distance (Å)^a

N-P ^b	${}^3\text{h}J_{\text{N}-\text{P}}$
3.92	-16.3
4.02	-13.0
4.11 ^c	-10.5
4.22	-7.9
4.37	-5.4
4.52	-3.6

^a These data are illustrated graphically in Figure 5. ^b The O-P distance in $\text{NH}_4^+:\text{OPH}_3$ is 1.521 Å. ^c The N-P distance in the optimized linear structure shown in Figure 1.

hydrogen bonds are dominated by the Fermi-contact term, which is distance dependent.^{6,7,10,11,14} Experimental studies of ${}^{31}\text{P}-{}^{31}\text{P}$ spin-spin coupling constants (${}^4\text{h}J_{\text{P}-\text{P}}$) across $\text{N}-\text{H}^+-\text{N}$ hydrogen bonds have also been reported.³⁵ Our theoretical studies have shown that four-bond ${}^{31}\text{P}-{}^{31}\text{P}$ coupling constants are also dominated by the distance-dependent Fermi-contact term.¹⁶ In the present study, we have computed PSO, DSO, FC, and SD contributions to three-bond N-P couplings across $\text{N}-\text{H}^+\cdots\text{O}-\text{P}$ hydrogen bonds for linear $\text{NH}_4^+:\text{OPH}$ in which the phosphorus is P(III), and for linear $\text{NH}_4^+:\text{OPH}_3$ in which the phosphorus is P(V). The results are reported in Table 3. These data show that the ${}^{15}\text{N}-{}^{31}\text{P}$ coupling constant involving P(III) is very small, with a value of only -0.3 Hz. In contrast, the ${}^{15}\text{N}-{}^{31}\text{P}$ coupling constant for P(V) is much larger at -10.9 Hz and is dominated by the Fermi-contact term at -10.5 Hz. For the P(V) complex, the PSO, DSO, and SD terms are more than an order of magnitude smaller than the Fermi-contact term. Therefore, the Fermi-contact term will be used to approximate ${}^3\text{h}J_{\text{N}-\text{P}}$.

Table 4 reports the distance dependence of the Fermi-contact term in linear $\text{NH}_4^+:\text{OPH}_3$. The value of ${}^3\text{h}J_{\text{N}-\text{P}}$ decreases significantly as a function of distance, from -16.3 Hz at an N-P distance of 3.92 Å, to -3.6 Hz at an N-P distance of 4.52 Å. There is a smooth decrease of ${}^3\text{h}J_{\text{N}-\text{P}}$ as a function of increasing N-P distance, as illustrated in Figure 5. Figure 5 can be used to predict N-P distances (and, therefore, hydrogen-bonding N-O distances) from experimental three-bond N-P spin-spin coupling constants in cationic complexes stabilized by $\text{N}-\text{H}^+\cdots\text{O}-\text{P}$ hydrogen bonds.

The coupling constants reported for $\text{NH}_4^+:\text{OPH}_3$ are obtained for the complex in which the N, H, O, and P atoms are constrained to be collinear. To what extent does ${}^3\text{h}J_{\text{N}-\text{P}}$ change if the phosphorus atom does not lie on the $\text{N}-\text{H}-\text{O}$ line? As we have previously indicated, Shirakawa et al.¹⁵ suggested that a linear arrangement of H, O, and P atoms is a prerequisite for a measurable ${}^3\text{h}J_{\text{N}-\text{P}}$. This suggestion was based on the fact that they observed a coupling constant only in the protein: nucleotide complex in which H, O, and P appear to be nearly

(35) Laynez, J.; Menéndez, M.; Velasco, J. L. S.; Llamas-Saiz, A. L.; Foces-Foces, C.; Elguero, J.; Molina, P.; Alajárin, M. *J. Chem. Soc., Perkin Trans. 2* **1993**, 709.

(34) Del Bene, J. E.; Jordan, M. J. T. *Int. Rev. Phys. Chem.* **1999**, *18*, 119.

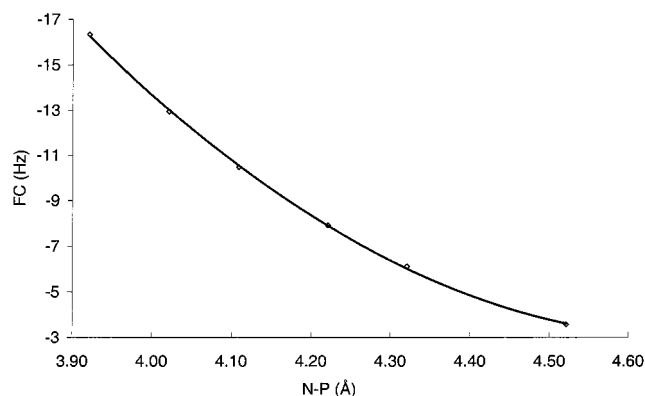


Figure 5. The distance dependence of the Fermi-contact term for linear $\text{NH}_4^+:\text{OPH}_3$ (see Figure 1). The optimized linear structure has an N–P distance of 4.11 Å.

Table 5. ${}^3\text{h}J_{\text{N-P}}$ (Hz) for $\text{NH}_4^+:\text{OPH}_3$ as a Function of the N–O–P Angle (deg)^{a–c}

$\angle\text{N-O-P}$	${}^3\text{h}J_{\text{N-P}}$
180 ^d	–5.4
170	–5.1
150	–3.6
130	–1.1
110	+0.9
90	–0.1

^a The N–O distance is 2.85 Å; the O–P distance is 1.52 Å. ^b The N–O–P angle was varied by rotation of OPH_3 about an axis through the O atom, and perpendicular to the symmetry plane of the complex. See Figure 1. ^c These data are illustrated graphically in Figure 6. ^d At $\angle\text{N-O-P} = 180^\circ$, N, H, O, and P are collinear.

collinear in the crystal structure, even though the N–O distance in that complex was not the shortest N–O distance. (It should be noted, however, that the crystal data for these complexes are limited by the accuracy of the atomic coordinates in the 2.2 Å structure and that the hydrogen atom in the hydrogen bond was added to the crystal structure using idealized covalent geometry.¹⁵) We have examined the angular dependence of ${}^3\text{h}J_{\text{N-P}}$ in $\text{NH}_4^+:\text{OPH}_3$. For this investigation, the hydrogen bond N–O distance is fixed at 2.85 Å, the N–O distance in the protein:nucleotide complex for which a coupling constant was measured in ref 15.

Table 5 shows the variation of ${}^3\text{h}J_{\text{N-P}}$ as a function of the N–O–P angle. (Because N, H, O, and P are collinear, the N–O–P angle is equal to the H–O–P angle.) These data are presented graphically in Figure 6. Table 5 and Figure 6 show that a small deviation from linearity is accompanied by only a small decrease in ${}^3\text{h}J_{\text{N-P}}$. Thus, a 10° deviation reduces ${}^3\text{h}J_{\text{N-P}}$ from –5.4 to –5.1 Hz. However, a 30° variation results in a 33% reduction of the coupling constant, which has a value of only –3.6 Hz when the N–O–P angle is 150°. An additional 30° decrease in the N–O–P angle reduces ${}^3\text{h}J_{\text{N-P}}$ to nearly zero. Thus, the N–P coupling constant decreases as the P atom is removed from the hydrogen-bonding axis. This occurs despite the fact that as the N–O–P angle decreases, the N–P distance also decreases. Thus, these results support the suggestion that a nearly linear N–H–O–P arrangement is required for a measurable three-bond ${}^{15}\text{N}$ – ${}^{31}\text{P}$ spin–spin coupling constant. That linear hydrogen bonds have larger coupling constants is also consistent with the results of previous studies of two-bond ${}^{17}\text{O}$ – ${}^{17}\text{O}$ and ${}^{15}\text{N}$ – ${}^{15}\text{N}$ coupling constants across O–H–O and N–H–N hydrogen bonds.^{11,14} Why a linear arrangement of

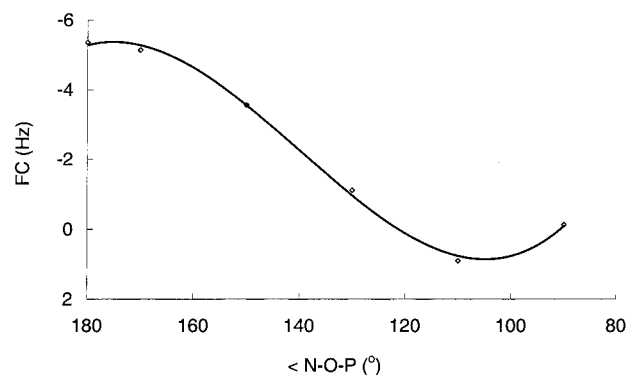


Figure 6. The Fermi-contact term for $\text{NH}_4^+:\text{OPH}_3$ as a function of the N–O–P angle. An angle of 180° corresponds to a linear arrangement of N, H, O, and P, as shown in Figure 1. Decreasing N–O–P angle corresponds to a counterclockwise rotation of OPH_3 about an axis through O and perpendicular to the symmetry plane. The N–O distance is 2.85 Å.

Table 6. N–P Distances (Å) and ${}^3\text{h}J_{\text{N-P}}$ (Hz) for Optimized Cyclic, Open, and Linear Anionic Complexes

complex	N–P	${}^3\text{h}J_{\text{N-P}}$
cyclic		
$\text{NH}_3^-\text{O}_2\text{PH}_2^a$	3.61	0.4
$\text{NFH}_2^-\text{O}_2\text{PH}_2$	3.47	0.6
open		
$\text{NH}_3^-\text{O}_2\text{PH}_2^b$	4.09	0.4
linear		
$\text{NH}_3^-\text{O}_2\text{PH}_2^c$	4.50	–1.9
$\text{NF}_2\text{H}^-\text{O}_2\text{PH}_2$	4.21	–4.7

^a The cyclic complex shown in Figure 2. ^b The open complex shown in Figure 3. ^c The linear complex shown in Figure 4.

coupled atoms across the hydrogen bond gives rise to a larger coupling constant is a question that remains to be answered. Table 6 reports N–P distances and ${}^3\text{h}J_{\text{N-P}}$ coupling constants for the anionic complexes which include two equilibrium cyclic complexes ($\text{NH}_3^-\text{O}_2\text{PH}_2$ and $\text{NFH}_2^-\text{O}_2\text{PH}_2$), the optimized open complex of $\text{NH}_3^-\text{O}_2\text{PH}_2$ which is stabilized by a single hydrogen bond, and two optimized linear complexes ($\text{NH}_3^-\text{O}_2\text{PH}_2$ and $\text{NF}_2\text{H}^-\text{O}_2\text{PH}_2$). The N–P distances in the cyclic complexes are 3.61 and 3.47 Å, respectively, but the N–P coupling constants are very small at 0.4 and 0.6 Hz, respectively. Similarly, ${}^3\text{h}J_{\text{N-P}}$ is only 0.4 Hz in the open $\text{NH}_3^-\text{O}_2\text{PH}_2$ complex in which the P atom does not lie along the hydrogen-bonding axis. In contrast, ${}^3\text{h}J_{\text{N-P}}$ values of –1.9 and –4.7 Hz are found for linear $\text{NH}_3^-\text{O}_2\text{PH}_2$ and $\text{NF}_2\text{H}^-\text{O}_2\text{PH}_2$, respectively, even though the N–P distances in these complexes are significantly longer at 4.50 and 4.21 Å, respectively. These data lend further support to the importance of a linear or nearly linear N–H–O–P arrangement for a measurable ${}^{15}\text{N}$ – ${}^{31}\text{P}$ coupling constant across an N–H···O–P hydrogen bond.¹⁵

Table 7 reports the distance dependence of ${}^3\text{h}J_{\text{N-P}}$ for linear $\text{NH}_3^-\text{O}_2\text{PH}_2$. These data are shown graphically in Figure 7. As is evident from this figure, ${}^3\text{h}J_{\text{N-P}}$ varies smoothly with distance. Figure 7 can be used to provide an estimate of N–P (and, therefore, hydrogen-bonding N–O) distances from experimentally measured three-bond spin–spin coupling constants across N–H···O–P hydrogen bonds. At an N–O distance of 2.85 Å, the computed value of ${}^3\text{h}J_{\text{N-P}}$ is –2.9 Hz. The absolute value of the computed coupling constant is smaller than the experimental value of 4.6 Hz reported in ref 15 for the protein:

Table 7. ${}^3\text{h}J_{\text{N-P}}$ (Hz) for Linear $\text{NH}_3\text{:}^-\text{O}_2\text{PH}_2$ as a Function of the N-P Distance (\AA)^a

N-P ^b	${}^3\text{h}J_{\text{N-P}}$
4.21	-5.2
4.26	-4.3
4.38	-2.9
4.50 ^c	-1.9
4.62	-1.3

^a These data are illustrated graphically in Figure 7. ^b The P-O distance is 1.530 \AA . ^c The N-P distance in the optimized linear structure illustrated in Figure 4.

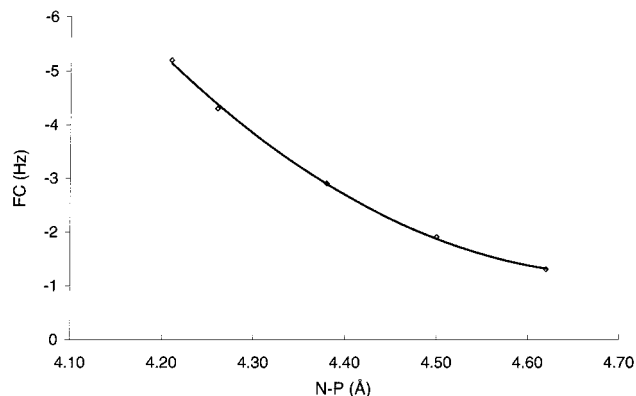


Figure 7. The distance dependence of the Fermi-contact term for linear $\text{NH}_3\text{:}^-\text{O}_2\text{PH}_2$ (see Figure 4). The optimized linear structure has an N-P distance of 4.50 \AA .

nucleotide complex with Ala18 and an α -phosphate group. However, given the accuracy of the 2.2 \AA crystal structure and the fact that the computed value of ${}^3\text{h}J_{\text{N-P}}$ at an N-O distance of 2.73 \AA is -4.3 Hz, the computed and experimental data are consistent. Moreover, the suggestion that coupling constants could not be measured for four of the five protein:nucleotide complexes investigated in ref 15 because of a nonlinear arrangement of H, O, and P atoms is consistent with the results of this study. Although the authors of ref 15 did not determine the sign of the N-P coupling constant, a negative value for

${}^3\text{h}J_{\text{N-P}}$ is reasonable taking into account the gyromagnetic factor of ${}^{15}\text{N}$.

Conclusions

This study supports the following conclusions.

(1) The ${}^{15}\text{N}-{}^{31}\text{P}$ coupling constant in $\text{NH}_4\text{:}^+\text{OPH}_3$ [with P(V)] is of sufficient magnitude to be measured experimentally, provided that N, H, O, and P atoms have a linear or nearly linear arrangement. The value of ${}^3\text{h}J_{\text{N-P}}$ for this complex is dominated by the Fermi-contact term, which is distance dependent. In contrast, ${}^3\text{h}J_{\text{N-P}}$ is negligible in $\text{NH}_4\text{:}^+\text{OPH}$ [with P(III)].

(2) The three-bond ${}^{15}\text{N}-{}^{31}\text{P}$ coupling constant for $\text{NH}_3\text{:}^-\text{O}_2\text{PH}_2$ is greatest in the optimized linear structure. ${}^3\text{h}J_{\text{N-P}}$ is negligible in the equilibrium cyclic structure which is stabilized by two distorted N-H \cdots O hydrogen bonds, and in an optimized open structure stabilized by a single hydrogen bond, despite the fact that the N-P distances in the cyclic and open structures are shorter than the N-P distance in the linear structure.

(3) ${}^3\text{h}J_{\text{N-P}}$ is distance dependent in linear anionic and cationic complexes. Thus, N-P (and, therefore, hydrogen-bonding N-O) distances can be determined for such complexes from experimentally measured coupling constants.

(4) The absence of a three-bond N-P coupling constant does not preclude the existence of an N-H \cdots O-P hydrogen bond, since a near linear arrangement of N, H, O, and P atoms is required for a measurable value of ${}^3\text{h}J_{\text{N-P}}$.

Acknowledgment. This work was supported by the National Science Foundation through grant CHE-9873815 (to J.E.D.B.), the Air Force Office of Scientific Research through grant F49620-98-1-0116 (to R.J.B.), and the Spanish DGICYT (projects BQU-2000-0252 and 0906). The continuing support of the Ohio Supercomputer Center is also gratefully acknowledged.

JA011755O