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$^{4h}J(^{31}P-^{31}P)$ Coupling Constants through N−H$^+$−N Hydrogen Bonds: A Comparsion of Computed ab Initio and Experimental Data

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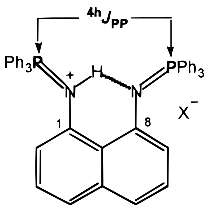
EOM-CCSD calculations have been performed to evaluate the $^{31}P-^{31}P$ coupling constant ($^{4h}J_{P-P}$) across an N−H$^+$−N hydrogen bond in a model system. Computed $^{4h}J_{P-P}$ values were obtained as a function of distance and are in agreement with an experimentally measured value of the $^{31}P-^{31}P$ coupling constant across an N−H$^+$−N hydrogen bond.

In recent years there has been significant interest and excitement about coupling constants across A−H−B hydrogen bonds.[1−15] These couplings are designated as two-bond couplings ($^{2h}J_{A-B}$) and four-bond couplings ($^{4h}J_{K-L}$) if K and L are bonded to A and B. Limbach,[2−4] Grzesiek,[5−7] Bax,[8,9] and Wüthrich[10] almost simultaneously described $^{2h}J(^{15}N-^{15}N)$, $^{2h}J(^{19}F-^{19}F)$, and $^{2h}J(^{15}N-^{19}F)$. Theoretical studies of coupling constants have also been reported,[2,7,11−14] including predictions of their values for N−H−N, N−H−O, and O−H−O prototypes.[12] The interest in coupling constants across hydrogen bonds lies in their potential usefulness for structure determination in biomolecules such as proteins and nucleic acids.[5,6,8,9]

In 1993, Laynez and co-workers[15] measured for the first time the $^{31}P-^{31}P$ coupling constant $^{4h}J(^{31}P-^{31}P)$ across a hydrogen bond in compound 1 (X = Br, PF$_6$). In the ^{13}C NMR spectrum the signal due to the carbon atoms C$_1$ and C$_8$ and the two phosphorus atoms appears as a quartet AA′XX′ pattern, with the peripheral transitions being twice as intense as the central ones. Analysis of this pattern yielded a coupling constant between the two phosphorus atoms [$^{4h}J(^{31}P-^{31}P)$] of about 3 Hz.

The same investigators[15] also determined the structures of the two molecules of compound **1** when X = Br (Cambridge structural database JODZAD) and X = PF$_6$ (JODZEH). In addition, the structure of the related compound in which one phenyl on each phosphorus is replaced by methyl and X is Br (JODZIL) has also been determined.[16] The N−N distances in these three compounds are 2.583, 2.604, and 2.535 Å, respectively, while the P−P distances are 5.156, 4.889, and 4.996 Å, respectively.

Perera and Bartlett have recently developed the equation-of-motion coupled cluster singles and doubles (EOM-CCSD)[17−20] method to compute NMR coupling constants. With this technique and Ahlrich's (qzp,qz2p) basis set,[21] it has been possible to compute from first principles NMR coupling constants which are in excellent agreement with known experimental data. Because of the uniqueness of the 4-bond coupling which was measured experimentally, we decided to apply these techniques to compute $^{4h}J(^{31}P-^{31}P)$ across an N−H−N hydrogen bond in the model cationic system, shown as structure **2**.



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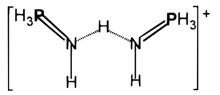

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It is not obvious whether the hydrogen bonds in compounds **1** are symmetric or not. In simple cationic systems, it has been observed[12,22] that the proton may be symmetrically bonded, or that the symmetric structure is a transition structure for proton transfer between two equivalent equilibrium structures of lower symmetry. In the latter case, the barrier to proton transfer may be below the zero-point vibrational energy, so that the symmetric structure is effectively the equilibrium structure. For this reason and for computational efficiency, we have optimized our model structure **2** at MBPT(2)[23−26] with the 6-31+G(d,p) basis set[27−30] under the constraint of C_{2v} symmetry with the proton symmetrically bonded to the two nitrogens. The optimized N−N distance in this model complex is 2.53 Å, while the P−P distance is 4.79 Å. The EOM-CCSD coupling constants have been computed using its CI-like approximation with Ahlrich's qzp basis set on N and P, and qz2p on the hydrogen-bonded proton. The basis set used for the remaining hydrogens is Dunnning's cc-pVDZ basis.[31,32] The coupling constants were computed using the ACESII program[33] on the SGI Origin computer at the Ohio Supercomputer Center.

Previous studies of $^{2h}J_{A-B}$ coupling constants across N−H−N, N−H−O, and O−H−O hydrogen bonds have shown that the coupling constant is dominated by the Fermi-contact term, and that this term is a function of the A−B distance.[12] In addition, $^{2h}J_{P-P}$ and $^{4h}J_{P-P}$ computed in several small hydrogen-bonded systems are also dominated by the Fermi-contact term. Therefore, we have computed only this term in order to estimate *J*. Moreover, since the optimized P−P distance in our model system is much shorter than the experimental P−P distances found in compounds **1**, we have computed $^{4h}J(^{31}P-^{31}P)$ as a

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TABLE 1: N−N and P−P Distances (Å) and Computed Coupling Constants [$^{4h}J(^{31}P-^{31}P)$ (Hz)] in the Model Structure 2[a]

N−N distance	P−P distance	$^{4h}J(^{31}P-^{31}P)$
2.53	4.79	14.3
2.83	5.09	8.1
3.03	5.29	5.9
3.33	5.59	3.9
3.53	5.79	3.0

[a] At all distances the N−H−N angle was held constant at 170°, the value in the optimized structure.

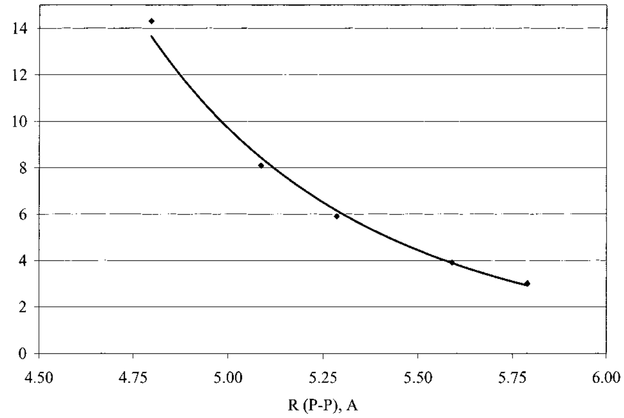

Figure 1. $^{4h}J(^{31}P-^{31}P)$ (Hz) versus the P−P distance (Å) in the model structure **2**.

function of the N−N distance (and therefore the P−P distance), keeping all other structural parameters fixed at their optimized values. The hydrogen bond in these structures is nearly linear, with an N−H−N angle of 170°. The N−N and P−P distances, and the coupling constants $^{4h}J(^{31}P-^{31}P)$ at these distances, are given in Table 1. The values of $^{4h}J(^{31}P-^{31}P)$ range from 14.3 Hz at a P−P distance of 4.79 Å, to 3.0 Hz at a distance of 5.79 Å. These data are plotted in Figure 1.

Given the difficulty both measuring experimentally and computing $^{4h}J(^{31}P-^{31}P)$, the agreement between theory and experiment is gratifying, even though the computed coupling constants suggest a longer P−P distance than measured experimentally. There are three factors which might account at least in part for the differences between theory and experiment. The first is that the model structure has a symmetrically-bonded proton. It has been shown that the A−B coupling constants across hydrogen bonds ($^{2h}J_{A-B}$) in cationic complexes are lower when the proton is not symmetrically bonded.[2,4,22] The proton position may also influence the value of ^{4h}J. The second factor is the replacement of the phenyl groups in the real molecule with hydrogens in the model cation. This should have some effect on the coupling constant, although it is not obvious whether J would increase or decrease. Finally, the experimental distances were determined in crystals, but the NMR data were obtained from solution studies. What effect the solvent might have is uncertain.

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