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Karplus-Type Equations for ^1J(X−Y) in Molecules H_mX-YH_n: (X, Y = N, O, P, S)

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Karplus-type equations are derived for the variation of one-bond X−Y coupling constants ^1J(X−Y) as a function of dihedral angle for molecules H_mX-YH_n, for X, Y, = ^{15}N, ^{17}O, ^{31}P, and ^{33}S. Coupling constants were obtained from ab initio EOM-CCSD calculations, with all terms evaluated. The relative orientation of lone pairs appears to be a primary factor determining the dependence of ^1J(X−Y) on the dihedral angle.

One of the most successful equations in NMR spectroscopy is the Karplus relationship, which relates the coupling constant ^3J(H−H) of an ethane fragment to the H−C−C−H dihedral angle.[1] This equation has the form $^3J(H-H) = a + b \cos\theta + c \cos^2\theta$, or $^3J(H-H) = a + b \cos\theta + c \cos 2\theta$.[2] If one considers the general case of an A−X−Y−B molecule with H−C−C−H as the reference, there are many possible variations, including the replacement of single by double bonds,[3] the replacement of the external hydrogen atoms by other atoms,[4] the replacement of the internal carbon atoms by other atoms,[5] or a combination of the two last modifications.[6]

The A−X−Y−B dihedral angle is determined by the orientation of A and B, but the coupling constants that depend on θ are not limited to ^3J(A−B), because ^2J(X−B), ^2J(A−Y),[7] or even ^1J(X−Y) is possible. It is this last coupling constant ^1J(X−Y) that is the focus of this Letter. Although not common, it is known that one-bond $^{31}P-^{31}P$ coupling in molecules of the type R_2P-PR_2 show a dependence on the orientation of the R groups.[8] There has also been a report on the dependence of one-bond $^{13}C-^{15}N$ coupling on the dihedral angles in proteins.[9] Finally, Serianni and Carmichael showed that ^1J(C−C) values depend not only on the C−C dihedral angle but also on other dihedrals.[10]

If the dependence of ^3J(A−B) coupling on the A−X−Y−B dihedral angle is intuitive, that of ^1J(X−Y) is not so obvious. Therefore, in this study we will examine the variation of ^1J(X−Y) with the dihedral angle for a series of molecules with the general formula H_mX-YH_n, for X, Y = ^{15}N, ^{17}O, ^{31}P, and ^{33}S. Because each of these molecules has 1 or 2 lone pairs of electrons on X and Y, it is not unreasonable to suggest that X−Y coupling constants may be sensitive to the relative orientation of the lone pairs, and that ^1J(X−Y) may vary significantly as the dihedral angle changes. The purpose of this Letter is to present X−Y coupling constants as a function of dihedral angle and derive Karplus-type equations for the variation of ^1J(X−Y).

TABLE 1: Distances (Å) and Angles (deg) for Molecules H_mX-YH_n

	distances			angles			
H_mX-YH_n	X−Y	X−H	Y−H	H−X−Y	X−Y−H	H−X−H	H−Y−H
H_2N-NH_2	1.460	1.015	1.015	107.5	107.5	106.0	106.0
H_2N-PH_2	1.763	1.013	1.417	110.6	98.0	106.1	91.8
H_2P-PH_2	2.252	1.414	1.414	95.0	95.0	92.6	92.6
H_2N-OH	1.452	1.017	0.966	101.9	103.4	106.2	
H_2N-SH	1.718	1.011	1.346	111.1	99.5	108.8	
H_2P-OH	1.670	1.417	0.963	99.6	110.0	92.4	
H_2P-SH	2.219	1.412	1.338	98.2	96.4	93.8	
HO−OH	1.477	0.970	0.970	100.0	100.0		
HO−SH	1.692	0.965	1.339	106.6	96.8		
HS−SH	2.099	1.338	1.338	95.5	95.5		

To obtain a reasonable set of fixed geometrical parameters for these molecules, structures were optimized at dihedral angles of 0° and 180°, and in some cases, the molecule was fully optimized, including the dihedral angle, when the equilibrium structure of the molecule did not correspond to a value of 0 or 180° for this angle. Then, average values of all internal coordinates for these structures were obtained and are reported in Table 1. These internal coordinates were fixed for subsequent calculations of coupling constants as a function of the dihedral angle. Geometry optimizations were carried out at second-order Møller−Plesset perturbation theory (MP2)[11−14] with the 6-31+G(d,p)[15−18] basis set for molecules in which X and Y are both second-period elements, and with the aug-cc-PVTZ[19,20] basis set for molecules containing P and/or S.

Ab initio spin−spin coupling constants were computed using the equation-of-motion coupled-cluster singles and doubles method (EOM-CCSD) in the CI(configuration interaction)-like approximation[21−24] with all electrons correlated, using the Ahlrichs[25] qzp basis set on N and O and the qz2p basis on H, P, and S. For these calculations, the dihedral angle (θ) was set to 0°, and then incremented to 180° in steps of 20°. At each value of θ the total coupling constant ^1J(X−Y) was evaluated as a sum of four terms: the paramagnetic spin−orbit (PSO), diamagnetic spin−orbit (DSO), Fermi-contact (FC), and spin-dipole (SD). Geometry optimizations were performed using Gaussian 03,[26] and coupling constants were evaluated using ACES II.[27] All calculations were carried out at the Ohio Supercomputer Center on the Cray X1 or the Itanium cluster.

The conformations of molecules H_mX-YH_n corresponding to a dihedral angle of 0° were defined as shown in Scheme 1.

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TABLE 2: Spin−Spin Coupling Constants $^1J(X-Y)$ (Hz) as a Function of Dihedral Angle θ (deg) for Molecules H_mX-YH_n

	0°	20°	40°	60°	80°	100°	120°	140°	160°	180°
H_2N-NH_2	−10.4	−10.3	−9.9	−8.9	−7.2	−5.2	−3.0	−1.1	0.2	0.7
H_2N-PH_2	52.6	52.3	50.8	46.9	40.6	32.5	23.8	15.7	9.8	7.5
H_2P-PH_2	−91.3	−99.0	−112.4	−114.3	−99.7	−74.1	−45.2	−19.3	−1.4	5.0
H_2N-OH	−17.7	−16.9	−14.8	−12.0	−9.1	−6.7	−4.8	−3.5	−2.7	−2.5
H_2N-SH	15.1	14.6	13.1	11.0	8.5	6.3	4.9	4.3	4.2	4.2
H_2P-OH	127.6	125.0	117.7	107.6	96.6	86.4	77.8	71.5	67.7	66.5
H_2P-SH	−47.7	−45.3	−39.2	−31.7	−25.3	−21.3	−19.1	−18.3	−18.1	−18.2
$HO-OH$	18.8	17.8	15.6	13.8	13.8	16.4	21.2	27.0	31.8	33.7
$HO-SH$	1.8	2.7	4.9	6.8	7.4	6.2	3.1	−0.9	−4.5	−6.0
$HS-SH$	8.6	7.4	4.5	1.8	0.4	0.8	2.9	6.4	9.7	11.1

SCHEME 1

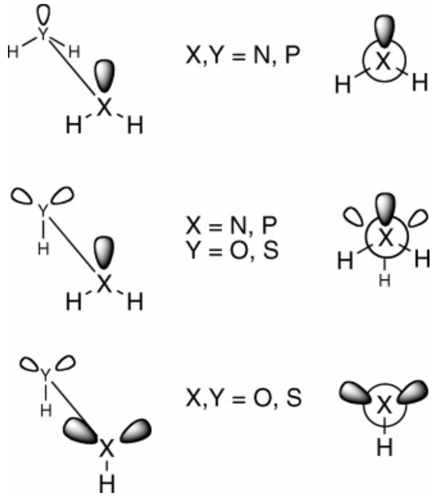

TABLE 3: Parameters for Karplus-Type Equations Relating $^1J(X-Y)$ (Hz) to the Dihedral Angle θ (deg) for Molecules H_mX-YH_n[a]

molecule	a	b	c	r^2[b]
H_2N-NH_2	−5.58	−5.64	0.70	1.000
H_2N-PH_2	33.58	22.7	−3.3	0.999
H_2P-PH_2[c]	−67	−54	23	0.985
H_2N-OH	−8.96	−7.49	−1.12	1.000
H_2N-SH	8.50	5.61	1.16	0.999
H_2P-OH	94.15	30.4	2.9	1.000
H_2P-SH	−27.9	−14.2	−5.0	0.998
$HO-OH$	20.42	−7.44	5.75	1.000
$HO-SH$	2.61	3.83	−4.59	0.999
$HS-SH$	4.88	−1.2	4.8	0.997

[a] The equations are $^1J(X-Y) = a + b\cos(\theta) + c\cos(2\theta)$. [b] r^2 is the correlation coefficient; $n = 10$ for each molecule. [c] The correlation coefficient improves to 0.999 when the next term in the expansion is added. The equation for H_2P-PH_2 becomes $^1J(P-P) = -67.4 + (-55.5)\cos(\theta) + 22.6\cos(2\theta) + 7.1\cos(3\theta)$.

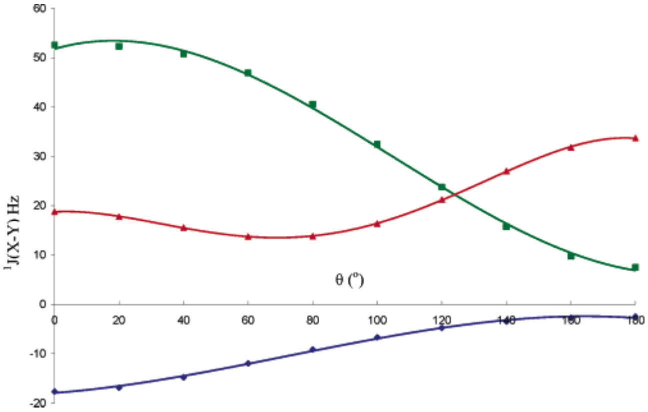

Figure 1. $^1J(X-Y)$ for H_2N-PH_2 (■), H_2N-OH (◆), and $HO-OH$ (▲) as a function of the dihedral angle θ.

For molecules H_2X-YH_2 and $HX-YH$, this orientation places the lone pairs in closest proximity cis with respect to the X−Y bond, and in an eclipsed conformation. For H_2X-YH the conformation at $\theta = 0°$ places the lone pairs cis with respect to the X−Y bond, with the lone pairs staggered but in closest proximity with the two lone pairs on Y equivalent. The values of $^1J(X-Y)$ as a function of dihedral angle for the 10 molecules investigated in this study are reported in Table 2.

From the values of Table 2, it is possible to construct Karplus-type equations for the variation of $^1J(X-Y)$ as a function of dihedral angle. The parameters a, b, and c, which define this equation for each molecule are given in Table 3, along with the values of the correlation coefficients, which are excellent for all molecules except H_2P-PH_2. However, if the next term is added to the series, an improved correlation coefficient of 0.999 is obtained, as reported in Table 3. Figure 1 presents curves showing the variation of coupling constant as a function of dihedral angle for molecules with 2 (H_2N-PH_2), 3 (H_2N-OH), and 4 ($HO-OH$) lone pairs, with at least 1 pair on each atom. [It should be noted that when comparing coupling constants involving different atoms, it is the reduced coupling constants $^1K(X-Y)$ which should be used, so that the dependence on the magnetogyric ratios of X and Y may be eliminated.] Neverthess, these curves, as well as the data of Table 3, indicate that changes in coupling constants as a function of dihedral angle may be large or relatively small, depending on the molecule. Moreover, because the magnetogyric ratios of N and O are negative and those of S and P are positive, the signs of coupling constants should be compared using reduced coupling constants. From the data of Table 2 it can be seen that the reduced coupling constants for all H_2X-YH_2 and H_2X-YH are negative for all dihedral angles, the exceptions being H_2N-NH_2 and H_2P-PH_2 as θ approaches 180°. These reduced X−Y coupling constants are therefore in violation of the Dirac Vector Model,[28] which states that all reduced one-bond coupling constants are positive. Both HO−OH and HS−SH have positive reduced coupling constants, whereas $^1J(S-O)$ for HO−SH changes sign.

Although not reported in this Letter, $^1J(X-Y)$ values as a function of dihedral angle were computed for H_3C-CH_3 with no lone pairs, and H_3C-OH and H_3C-SH (two lone pairs on O and S). For these molecules, although $^1J(X-Y)$ may be relatively large (+37.0, +13.9, and −5.7 Hz, respectively, at $\theta = 0°$), the variation in coupling constants as a function of θ is only about 0.5 Hz. [The experimental value of $^1J(C-C)$ for H_3C-CH_3 is 34.6 Hz.[29]] This supports our supposition that it is the presence of one or more lone pairs of electrons on X and Y that is responsible for the variation of $^1J(X-Y)$ with dihedral angle.

Unfortunately, there is a scarcity of experimental data for comparison, and no data are available for any of the molecules investigated in this work. The closest molecules are (C_6H_5)-

HN−NH_2, for which the experimental $^{15}N-^{15}N$ coupling constant is −6.7 Hz.[30] This corresponds to a value of $\theta = 84°$ from the Karplus equation for H_2N-NH_2. $^1J(P-N)$ have been measured for $(CH_3)_2N-P(CH_3)_2$ (60 Hz) and $(C_6H_5)HN-PH(C_6H_5)$ (53 Hz).[31] These correspond to $^1J(P-N)$ values calculated at small dihedral angles. Finally, P−P coupling constants for $(CH_3)_2P-P(CH_3)_2$ (−180 Hz) and $(C_6H_5)HP-PH(C_6H_5)$ (−191 Hz) have been measured.[32] Because our largest value for H_2P-PH_2 is only −114 Hz, either these calculations significantly underestimate P−P coupling or the substituents significantly increase the P−P coupling constant.

In summary, these results show that changes in one-bond X−Y coupling constants as a function of dihedral angle for molecules H_mX-YH_n having at least one lone pair of electrons on X and Y follow Karplus-type behavior. A detailed analysis of the signs and magnitudes of the terms that contribute to the coupling constants, the variation of the Fermi-contact term with dihedral angle, and relationships among reduced X−Y coupling constants will be the subject of a future paper.

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