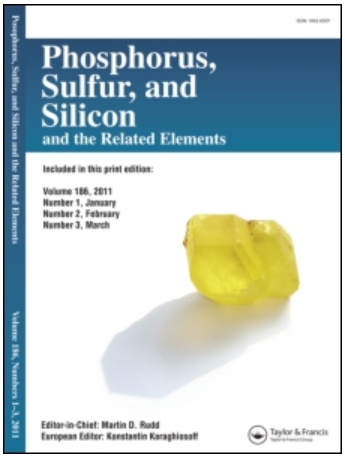


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Physical Image vs. Structure Relation, Part 13[1]: Calculational Evidences for the ^{2}h J_{PH} Spin-Spin Coupling in Internally H-Bonded Isomers of Some 1-Oxoalkanephosphonate Hydrazones

Ryszard B. Nazarski[a]
[a] Department of Organic Chemistry, Faculty of Chemistry, University of Łódź, Łódź, Poland

To cite this Article Nazarski, Ryszard B.(2009) 'Physical Image vs. Structure Relation, Part 13[1]: Calculational Evidences for the ^{2}h J_{PH} Spin-Spin Coupling in Internally H-Bonded Isomers of Some 1-Oxoalkanephosphonate Hydrazones', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 4, 1036 — 1046
To link to this Article: DOI: 10.1080/10426500902737349
URL: http://dx.doi.org/10.1080/10426500902737349

Phosphorus, Sulfur, and Silicon, 184:1036–1046, 2009

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500902737349

Taylor & Francis
Taylor & Francis Group

Physical Image vs. Structure Relation, Part 13[1]: Calculational Evidences for the $^{2h}J_{PH}$ Spin–Spin Coupling in Internally H-Bonded Isomers of Some 1-Oxoalkanephosphonate Hydrazones

Ryszard B. Nazarski
Department of Organic Chemistry, Faculty of Chemistry, University of Łódź, Łódź, Poland

The P(IV)↔H spin–spin transfer across the N—H···O$^-$–P$^+$ intramolecular H-bond previously observed NMR spectroscopically for Z *stereoisomers of hydrazones of* O,O′*-diisopropyl 1-oxoalkanephosphonates,* $^{2h}J_{PH} = 2.95 \pm 0.35$ *Hz, was rationalized using Fermi-contact (FC) contributions to such* J_{PH} *couplings. Moreover, the FC terms were found to be dominant terms of these* $^{2h}J_{PH}$ *couplings. The applied FPT-DFT(B3LYP) FC calculational approach was successfully tested on* J_{PH} *couplings in model phosphorus esters. As a result, linear relation* J_{PH}^{obsd} *(*$CDCl_3$*) vs.* $J_{PH}^{FC\,calcd}$ *was established for different long-range* J_{PH} *couplings occurring via an oxygen atom of the phosphoryl group.*

Keywords Conformations; Fermi-contact term; FPT-DFT method; indirect $^{2h}J_{PH}$ coupling across intramolecular H-bond; NMR spectroscopy; phosphorus esters

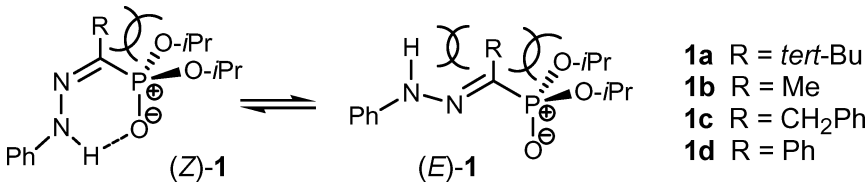
INTRODUCTION

High-resolution NMR spectroscopy is an extremely powerful tool for studies of diamagnetic species, including a wide variety of chemical compounds. It enables probing the structure, dynamics, and conformational preference of such species, especially in solution. Currently, these possibilities became considerably enhanced for common spin-1/2 nuclei X by the application of two supporting methods of computational chemistry, i.e., the GIAO prediction of chemical shifts, δ_Xs, and DFT evaluation of indirect nuclear spin–spin coupling constants, $^nJ_{AB}$

Received 8 January 2008; accepted 11 February 2008.

Dedicated to Professor Marian Mikołajczyk from the CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

Address correspondence to Ryszard B. Nazarski, Laboratory of Molecular Spectroscopy, Faculty of Chemistry, University of Łódź, Narutowicza 68, 90-136 Łódź, Poland. E-mail: rymaja@uni.lodz.pl



SCHEME 1 Dynamic equilibrium involving the investigated hydrazones **1** (except the *tert*-butyl system **1a** for which only the *H*-bonded *Z* stereoisomer was observed, due to sterical hindrance).

couplings.[2] The δ_X values are strongly sensitive to their molecular environment, thereby providing insight into local functionality and stereochemistry. In turn, information about the electronic structure of the whole molecule and spatial arrangements of interacting nuclei is accessible via the second main NMR parameter (*J* coupling).

Eight years ago, we reported[3] on appeared P(IV)↔H couplings $^{x}J_{PH}$ of 2.95 ± 0.35 Hz, involving the N—H protons in *Z* forms of some *O*,*O*′-di*iso*propyl 1-oxoalkane phosphonate phenylhydrazones **1a**–**d** (Scheme 1, Table I), which were studied in detail using ^{1}H, ^{13}C, and ^{31}P multinuclear magnetic resonance spectroscopy in solution.[3–5] (We strongly prefer a representation of the phosphoryl group by the $O^{-}-P^{+}$ and not the O=P mesomeric form, according to theoretical considerations.[6]) The possibility of a spin-polarization transfer across the stabilizing N—H···$O^{-}-P^{+}$ intramolecular hydrogen bond (H-bond), observed for the first time in the case of such NMR active nuclei, was considered during our research.[3]

TABLE I FC Terms and J_{PH} Couplings Evaluated for the B3LYP/6-31G Structures of *E*- and *Z*-Stereoisomers of Hydrazones 1, in Hz**

	R	J_{PH}^{obsd} (in $CDCl_3$)[a]	$J_{PH}^{FC\,calcd}$ (in vacuo)[b]	$J_{PH}^{FC\,calcd}$ (in vacuo)[c]	$J_{PH}^{total\,calcd}$ (in vacuo)[d,e]	$J_{PH}^{total\,pred}$ (in $CDCl_3$)[f]
(*Z*)-**1a**	*tert*-Bu	3.3	+3.77	+3.77	+4.15	+3.62
(*Z*)-**1b**	Me	3.2	+3.62	+3.65	+3.94	+3.47
(*Z*)-**1c**	CH_2Ph	2.9	+3.41	+3.44	+3.73	+3.26
(*Z*)-**1d**	Ph	2.6	+3.42	+3.45	+3.71	+3.27
(*E*)-**1b**	Me	*g*	+0.80	*h*	+1.39	*h*

[a]Absolute values experimentally measured[3,4] for both isomers in the *E*/*Z* mixture (excluding **1a**); [b]spin perturbation placed on the *H*-bonded proton[4c]; [c]spin perturbation placed on the P nucleus[4c]; [d]predicted using Gaussian 03 (all four Ramsey's terms considered); [e]the FC term was found as identical with that FPT computed according to footnote[b]; [f] estimated with the scaling relationship given in ref.[20]; [g]not detected; [h]not computed.

Our communication on $^{x}J_{PH}$ couplings in hydrazone systems (*Z*)-**1** was subsequently followed by two independent findings of H-bond–mediated $^{2h}J_{PH}$ couplings concerning phosphorus nuclei in a protein-nucleotide complex[7] and in *D. vulgaris* flavodoxin (as a flavoprotein).[8] Such experimentally measured NMR data as reported by Mishima et al.[7] were supported later by deMon-NMR code-based DFT prediction[9] of these $^{2h}J_{PH}$ couplings carried out for two simple models of two large biomolecular fragments of the complex mentioned above.

In this article, we report theoretical evidence for the $^{2h}J_{PH}$ coupling in the hydrazone esters (*Z*)-**1**. The computational approach based on a current variant of the finite perturbation theory (FPT)-DFT method was applied for this purpose, owing to the relatively large molecular size of the investigated compounds. Thus, the total J_{PH} couplings have been estimated solely from the Fermi-contact (FC) terms. However, FC terms were found to be the most important contributions to $^{2h}J_{PH}$ couplings in these systems. Moreover, the reliability of such a simplified FC approach was successfully tested on literature data concerning some model phosphorus esters.

RESULTS AND DISCUSSION

In principle, three possibilities exist for molecules (*Z*)-**1** to explain the $^{x}J_{PH}$ couplings in question, namely (*i*) heteronuclear P(IV)↔H interactions, i.e., ^{2h}J couplings occurring via internal H-bridges of the N—H···O^{-}—P^{+} type in practically planar six-membered ring systems; (*ii*) long-range four-bond coupling (^{4}J) along a molecular backbone; and (*iii*) simultaneous participation of these both mechanisms. One should expect that spin polarization is more effectively transmitted via a "through-backbone" way (*ii*) in compounds (*E*)-**1**, owing to the favorable *trans* arrangement around the N=C bond in these systems. As a consequence, absolute values of the pure traditional $^{4}J_{PH}$ coupling should also be greater for these species. So, we came to the conclusion that the best way to choose between the possible mechanisms is to use an adequate theoretical approach involving both configurations of hydrazones **1**.

FC terms are usually the most dominant contributors to the total $^{n}J_{AB}$ couplings, including spin–spin interactions with phosphorus nuclei.[10] Indeed, the other three Ramsey's contributions to *J*-couplings, i.e., non-FC mechanisms, have been shown to be generally much smaller and less dependent on structural variation.[11] Therefore, a single-FC-perturbation DFT variant[12] of the FPT method originally

introduced by Pople et al.[13] was used here to economically recover FC contributions to $^{x}J_{PH}$ couplings of interest.

Accordingly, adequate initial molecular modeling and subsequent quantum chemical calculations of J_{PH} couplings were performed; cf. the Experimental section. Final results obtained within the programs Gaussian 98[14] and Gaussian 03[15] (for comparison reasons, vide infra) are given in Table I, together with the measured J values.[3,4] In order to control the mutual consistency of the J data computed in this way, $^{3}J_{POCH}$ unambiguously evaluated from the ^{31}P NMR spectrum of the sole observed Z isomer of *tert*-butyl hydrazone **1a** was also predicted (see Figure 1). For two different orientations of its methine protons in space (and so different P—O—C—H dihedral angles of 30.8° and –35.6°), related $^{3}J_{POCH}$ couplings were found[4b,d] in solution as time-averaged to 7.8 Hz, in good agreement with $J_{PH}^{FC calcd} = 8.21$ Hz. A standard 6-31G** basis set was used in final J_{PH} calculations owing to the relatively large molecular size of the studied objects. However a valence basis set of double-ζ quality was recommended[16] as an optimum trade for accuracy versus cost for such purposes. Moreover, as far we are aware, the FPT-DFT approach of this kind (especially, concerning the 6-31G** basis set

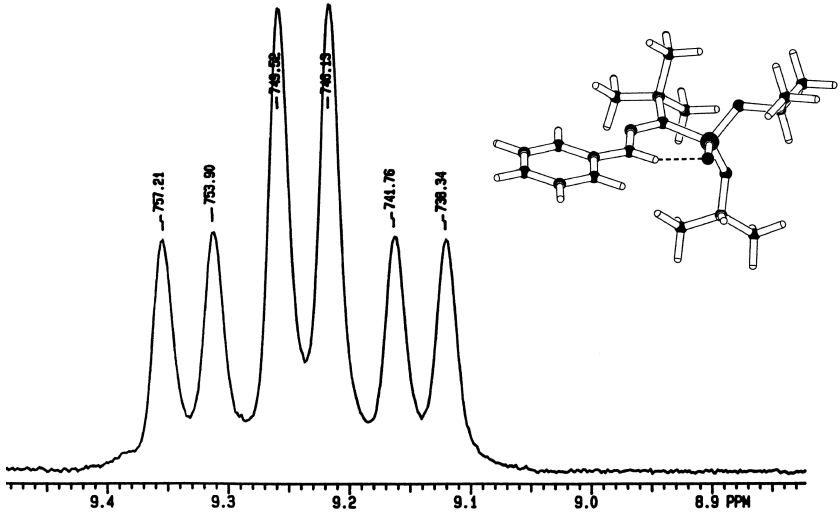
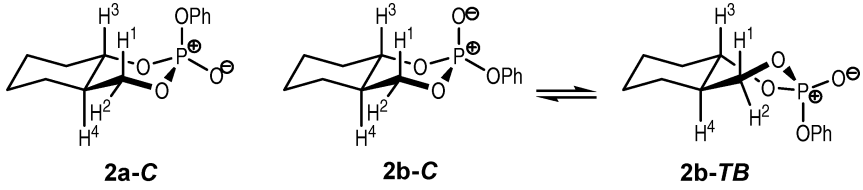


FIGURE 1 The 80.95 MHz proton coupled ^{31}P NMR spectrum (in $CDCl_3$ at ~21°C) of Z form of hydrazone **1a** (R = *tert*-butyl); $\delta_P = 9.24$ ppm, $^{3}J_{POCH} = 7.8$ Hz, $^{2h}J_{P-O^{-}\cdots H} = 3.3$ Hz.[4d] The PLUTON drawing of its B3LYP/6-31G**-optimized structure with the stabilizing N—H···O^{-}—P^{+} intramolecular hydrogen bond is given above.

and magnitude of the perturbation parameter λ of 0.01) was previously not applied for phosphorus compounds. Indeed, in the foregoing small molecule FC calculations[9] a rather large Iglo-III basis set and $\lambda = 0.001$ at the position of the ^{31}P nucleus were used.

Our approach was fully justified by successful reproduction of various long-range J_{PH} couplings for an epimeric pair of cyclic phosphate triesters **2** previously studied in $CDCl_3$ solution by Gorenstein et al.[17] In fact, a very strong (not shown) linear relationship $J_{PH}^{\text{total pred}}$ [Hz] = 0.9900 $J_{PH}^{\text{FC calcd}}$ + 0.1383 ($r = 0.9977$, $SD = 0.32$ Hz, $N = 8$) was found between $J_{PH}^{\text{FC calcd}}$ couplings and experimentally measured J_{PH} couplings for the conformationally rigid compound **2a**–*C* and flexible compound **2b**, which were used as test phosphorus systems (Scheme 2). For the latter, about 24% contribution of a twist-boat form **2b**-***TB*** was estimated for rapid dynamic equilibration between two associated conformers by applying the in vacuo–computed FC terms. This result is in line with 49% and 78% presence of **2b**-***TB*** originally estimated[17a] for $CDCl_3$ and CH_3OH solution, respectively. Interestingly, all five *J*-value points $\{J_{PH}^{\text{FC calcd}}, J_{PH}^{\text{obsd}}\}$ established earlier for the hydrazones (*Z*)-**1** fulfil



$^3J_{PH1}^{obsd}$ = 0 Hz
$^3J_{PH2}^{obsd}$ = 24.4 Hz
$^3J_{PH3}^{obsd}$ = 1.0 Hz
$^4J_{PH4}^{obsd}$ = 0.0 Hz

$^3J_{PH1}^{obsd}$ = 5.5 Hz
$^3J_{PH2}^{obsd}$ = 18.5 Hz
$^3J_{PH3}^{obsd}$ = 2.0 Hz
$^4J_{PH4}^{obsd}$ = 0.0 Hz

$J^{FC}_{PH1}{}^{calcd}$ = **0.75** Hz
$J^{FC}_{PH2}{}^{calcd}$ = **23.72** Hz
$J^{FC}_{PH3}{}^{calcd}$ = **1.19** Hz
$J^{FC}_{PH4}{}^{calcd}$ = **-0.62** Hz

$J^{FC}_{PH1}{}^{calcd}$ = 1.09 Hz
$J^{FC}_{PH2}{}^{calcd}$ = 25.17 Hz
$J^{FC}_{PH3}{}^{calcd}$ = 1.61 Hz
$J^{FC}_{PH4}{}^{calcd}$ = -0.51 Hz

$J^{FC}_{PH1}{}^{calcd}$ = 19.45 Hz
$J^{FC}_{PH2}{}^{calcd}$ = 0.91 Hz
$J^{FC}_{PH3}{}^{calcd}$ = 0.42 Hz
$J^{FC}_{PH4}{}^{calcd}$ = -0.22 Hz

for ~24% of **2b**-***TB***:
$J^{FC}_{PH1}{}^{calcd}$ = **5.40** Hz
$J^{FC}_{PH2}{}^{calcd}$ = **19.47** Hz
$J^{FC}_{PH3}{}^{calcd}$ = **1.33** Hz
$J^{FC}_{PH4}{}^{calcd}$ = **-0.44** Hz

SCHEME 2 FC contributions to selected couplings $^3J_{PH}$ and $^4J_{PH}$ in test phosphorus systems **2**.[17] The ~24 % contents of **2b**-*TB* were presently found under conditions of the best correlation.

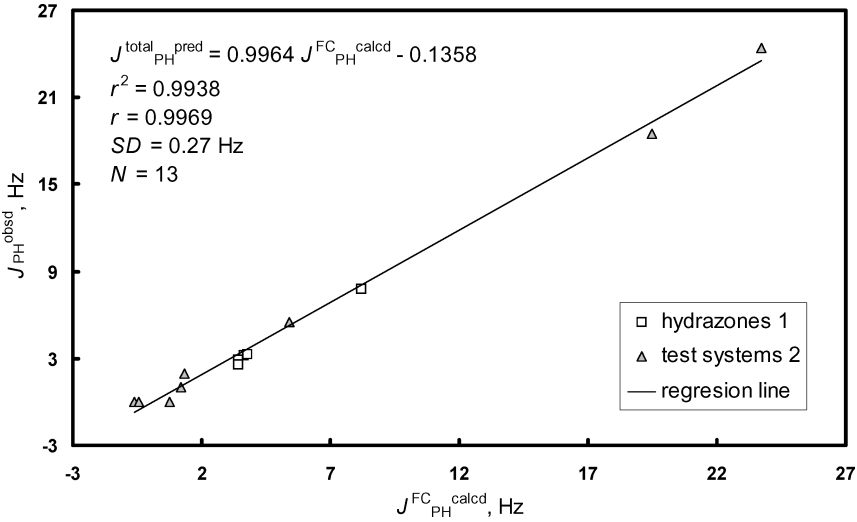


FIGURE 2 Scatter plot of the relation J_{PH}^{obsd} ($CDCl_3$) vs. $J_{PH}^{FCcalcd}$ from linear regression analysis of the FPT-DFT(UB3LYP/6-31G**//RB3LYP/6-31G**) results for various long-range J_{PH}couplings across the oxygen atom in compounds **1a–d** and **2a–b**; calculated J values are taken from Table I (spin perturbation placed on the *H*-bonded proton) and Scheme 2 (numbers in boldface type).

very well the aforementioned relationship found for the phosphates **2** alone. A new relationship covering 13 of the *J*-data points for all of discussed compounds (*Z*)-**1** and **2** is given with pertinent statistics in Figure 2. The resulting slope of 0.996 and intercept of −0.136 are worth being mentioned, as they are very close to their ideal values of 1 and 0, respectively.

In sharp contrast to the aforementioned, only a small value of the FC contribution to the total $^4J_{PH}$ coupling was predicted for the only analogously studied *E* stereoisomer of hydrazones **1**, i.e., for the smallest molecule *E*-**1b**. Indeed a coupling $^4J_{PH}^{FCcalcd}$ of only 0.80 Hz was calculated for it vs. $^2J_{PH}^{FCcalcd} = 3.62$ Hz found for its counterpart (*Z*)-**1b** (Table I). This is in full agreement with the experiment, because in no case was a J_{PH} coupling for the species (*E*)-**1b**–**d** experimentally observed.[4] In other words, this result indicates that $^xJ_{PH}$ couplings of ~3.0 Hz previously determined in $CDCl_3$ for compounds (*Z*)-**1** are in fact due to H-bond–mediated $^{2h}J_{PH}$ coupling occurring via an accepting oxygen nucleus of the phosphoryl group.

Alternatively, the FC term of 0.80 Hz found for (*E*)-**1b** comprises only 58% of the pertinent total $^4J_{PH}$ coupling computed with Gaussian 03[15] at an adequate level of theory (Table I). This finding strongly indicates

that the noncontact terms are important for such spin–spin interactions in hydrazones (*E*)-**1**, in agreement with the data in the literature for multiply bonded systems.[11a] Therefore, care must be taken if J_{PH} couplings occurring via this kind of bond(s) are investigated, because all four contributions to such couplings should be evaluated. However this is not the case for J_{PH} couplings in *H*-bonded *Z*-isomers of species **1**, for which the FC terms amounts to about 91.5% of the total $^{2h}J_{PH}$ coupling. Indeed, this finding is in accord with previous results of Del Bene et al.,[18] which found that that couplings $^{nh}J_{AB}$ (n = 2 or 3) across hydrogen bonds of the type A—H···B or A—H···O—B are largely dominated by their FC components.

A very strong correlation ($r = 0.9969, SD = 0.27$ Hz, $N = 13$; Figure 2) established in this work for two different types of P(IV)↔H interactions across an intervening oxygen atom, i.e. concerning various long-range couplings $^{2h}J_{P-O-\cdots H}$, $^{3}J_{P-O-C-H}$ and $^{4}J_{P-O-C-C-H}$, is most likely of a more general nature. Indeed, its application for *O*,*O*′-dimethyl methylphosphonate [$CH_3P(O)(OCH_3)_2$, **3**, not used in evaluation of the above relation, afforded $J_{PH}^{FC\,calcd} = 11.27$ Hz and hence $J_{PH}^{total\,pred} = 11.09$ Hz, in excellent agreement with $^{3}J_{PH}$ of 11.0 Hz recently found[19] in $CDCl_3$ solution. Undoubtedly, additional investigations are needed in this field.[20]

Let us turn our attention to the performed *J*-coupling calculations. When implementing a single FC perturbation variant of the FPT method applied here, i.e., the FPT-1 version, care must be taken that the computed *J* values do not depend either on the size of used FC perturbation λ or on which of both coupled nuclei this fine perturbation is placed.[12c] However, it was suggested that for such heteronuclear J_{AB}^{FC} term calculations it is preferable to place the perturbation at the lighter nucleus (usually proton) rather than at the heavier nucleus site.[11b,12a,c] In our hands, only slightly lower (by 0.03 Hz) J_{PH}^{FC} values were computed for hydrazones **1b–d** using the letter proposal, whereas for *tert*-butyl compound **1a** the two results were identical (Table I). Thus, both requirements mentioned above are fulfilled in practice.

EXPERIMENTAL

NMR Spectroscopy

The ^{31}P and $^{31}P\{^{1}H\}$ NMR spectra of hydrazones **1**, obtained following the reported method,[21] were recorded with a Varian Gemini 200 BB spectrometer operating at 80.95 MHz. All of the measurements were carried out at room temperature (ca. 21°C) for dilute solutions

in $CDCl_3$ as a deuterated solvent. Coupling constants J are reported in Hz. These values were directly evaluated from the proton-coupled ^{31}P NMR spectra (see Figure 1), because very broad and usually poorly resolved doublets due to *P*-coupled intramolecularly bonded N—H protons were observed in the related ^{1}H NMR spectra.[22] Chemical shifts are expressed in the δ units [ppm] positive downfield from 85% H_3PO_3 applied as an external reference standard ($\delta_P = 0$ ppm); no magnetic susceptibility correction was used.

Calculational Details

Molecular Modeling

The conformational search for minima on the potential energy surfaces (PES) of isolated species **1–3** was performed with MMX force field calculations, using the GMMX routine within PCMODEL.[23] A mixed molecular-mechanics searching protocol was employed with randomization over all rotatable bonds. Typically, 700–1500 steps were employed within the 14.6 kJ mol^{-1} energy window; a bulk value of the relative permittivity (dielectric constant) was used for the gas phase, $\varepsilon = 1.50$.[24] The ensuing variety of conformational structures, usually of approximately five unique structures of every molecule, were subsequently applied as trial input configurations in the geometry optimization using the semi-empirical PM3 hamiltonian of HyperChem.[25] The resulting low-energy forms were next subjected to further fully relaxed geometry refinement at the ab initio restricted HF level of theory using two standard Pople's basis sets: initially 3-21G[26] and then 6-31G*. Final in vacuo energy minimization was carried out by applying a double-ζ plus polarization basis set 6-31G** (with six, not five d wave functions used for all non-H atoms) in conjunction with the HF-DFT hybrid B3LYP,[27] functional as implemented in the Gaussian code. In addition, harmonic vibrational frequencies were computed at the 6-31G* level of theory to confirm that each located energy minimum is an equilibrium structure on related DFT-based PESs (no imaginary frequencies). Molecules were visualized by applying the PLUTON option within PLATON[28] for Windows using the PCMODEL outputs.

J-Coupling Calculations

Low-energy structures located in the aforementioned way were subsequently used in a single-point prediction of J couplings. More precisely, only their isotropic FC components were computed within Pople et al.'s[13] finite perturbation theory (FPT) approach[12] using a single-

perturbation DFT formalism at the UB3LYP/6-31G**// RB3LYP/6-31G** level of theory. These Fermi-contact terms were recovered indirectly from FC outputs of the FIELD option of Gaussian 98.[14] The spin perturbation of 10^{-2} au was applied on the N–H proton (or on the P nucleus, see text) to obtain all couplings to this nucleus, as was recommended by Bagno[29] in the case of weak J couplings. In addition, a TIGHT criterion of the SCF convergence was always employed. Finally, the FC component of each J_{PH} coupling (generally J_{AB} coupling) was calculated using Equation (1), which was adopted from Bagno[29]:

$$J_{AB}^{FC} = constant\ \frac{\gamma_A \gamma_B}{\lambda} B_{AB}^{FC} \quad (1)$$

where $constant = 1.058297 \times 10^{-10}$, γ_A and γ_A are the magnetogyric ratios of the involved NMR nuclei, λ—the applied FC perturbation in atomic units (au), and B^{FC}—the calculated FC term, in au. Since we are concerned with the $^{31}P-^{1}H$ couplings only ($\gamma_P = 1.08394 \times 10^8\ s^{-1}T^{-1}$ and $\gamma_H = 2.67522 \times 10^8\ s^{-1}T^{-1}$)[29,30] all of the quantities in Equation (1) are defined and, consequently, J_{PH}^{FC} [Hz] $= 30688.25\ B_{PH}^{FC}$, if $\lambda = 10^{-2}$au.

The same FC term values (see, footnote *e* in Table I) are directly available at the RB3LYP/6-31G**//RB3LYP/6-31G** level of theory using Gaussian 03,[15] which allow calculation of all four Ramsey's contributions to J couplings. Statistical analysis was carried out by the MS Excel 97 spreadsheet.

CONCLUSION

The present computations show that P↔H spin–spin interactions previously observed in the ^{1}H and ^{31}P NMR spectra of the hydrazones (*Z*)-**1** are in fact due to $^{2h}J_{PH}$ couplings across the N–H···O$^-$–P$^+$ intramolecular H-bonds. The Fermi-contact terms were found to be the most important for $^{2h}J_{PH}$ couplings in such molecules. A current single FC perturbation variant of the FPT-DFT method used for these systems afforded only negligibly smaller ($\leq$0.03 Hz) FC-derived $^{2h}J_{PH}$ couplings when a spin perturbation was (preferentially) placed on *H*-bonded protons. Linear relationship J_{PH}^{obsd} ($CDCl_3$) vs. $J_{PH}^{FC\,calcd}$ (vacuum) was determined for various types of long-range NMR J_{PH} couplings transmitted via the oxygen atom of the phosphoryl group. However, it is necessary to be careful using this simplified FC procedure for prediction of J_{PH} couplings occurring via multiple bond(s), e.g., the C=N–N unit in isomers (*E*)-**1**. In these cases all four Ramsey's terms should be evaluated.

REFERENCES

[1] Part 12: R. B. Nazarski, *J. Phys. Org. Chem.*, **20,** 422 (2007).

[2] See, e.g., (a) T. Helgaker, M. Jaszuński, and K. Ruud, *Chem. Rev.,* **99,** 293 (1999); (b) C. van Wüllen, in *Calculation of NMR and EPR Parameters*: *Theory and Applications*, M. Kaupp, M. Bühl, and V. G. Malkin, Eds. (Wiley-VCH, Weinheim, 2004), pp. 85–100; (c) T. Helgaker and M. Pecul, in *Calculation of NMR and EPR Parameters*: *Theory and Applications*, M. Kaupp, M. Bühl, and V. G. Malkin, Eds. (Wiley-VCH, Weinheim, 2004), pp. 101–121.

[3] R. B. Nazarski, D. K. Gralak, and Z. H. Kudzin, *Bull. Pol. Acad. Sci., Chem.*, **48,** 27 (2000).

[4] (a) D. K. Gralak, Z. H. Kudzin, and R. B. Nazarski, poster presented at the *Symposium on an Application of Magnetic Resonance in Chemistry and Related Areas*, Warszawa, June 25–27, 1997, abstract P-35; (b) D. K. Gralak, Master Thesis, University of Łódź, Łódź, Poland (1997); (c) R. B. Nazarski, poster presented at *the XXXVI Polish Seminar on NMR and Its Applications*, Kraków, December 1–2, 2003, Abstracts, pp. 62–63; (d) R. B. Nazarski, unpublished results.

[5] Recently, the *E* form of the hydrazone **1c** was erroneously reported as (*Z*)-**1c**: Z. Hassen, A. Ben Akacha, and H. Zantour, *Phosphorus, Sulfur, and Silicon,* **178,** 2241 (2003). Its physico-chemical data (mp, NMR) were found as practically identical with those determined for the product (*E*)-**1c** isolated chromatographically.[4b] ^{1}H and ^{31}P{^{1}H} NMR spectra of an equilibrated *E*/*Z* (47 : 53) isomeric mixture of **1c** were published in ref.[3]

[6] L. Chęcińska, Z. H. Kudzin, M. Małecka, R. B. Nazarski, and A. Okruszek, *Tetrahedron*, **59,** 7681 (2003).

[7] M. Mishima, M. Hatanaka, S. Yokoyama, T. Ikegami, M. Wälchli, Y. Ito, and M. Shirakawa, *J. Am. Chem. Soc.*, **122,** 5883 (2000).

[8] F. Löhr, S. G. Mayhew, and H. Rüterjans, *J. Am. Chem. Soc.*, **122,** 9289 (2000).

[9] J. Czernek and R. Brüschweiler, *J. Am. Chem. Soc.*, **123,** 11079 (2001).

[10] O. L. Malkina, D. R. Salahub, and V. G. Malkin, *J. Chem. Phys.*, **105,** 8793 (1996), and references cited therein.

[11] (a) J. Geertsen, J. Oddershede, and G. E. Scuseria, *J. Chem. Phys.*, **87,** 2138 (1987); (b) V. G. Malkin, O. L. Malkina, and D. R. Salahub, *Chem. Phys. Lett.*, **221,** 91 (1994).

[12] (a) G. Cuevas, E. Juaristi, and A. Vela*, J. Phys. Chem. A*, **103,** 932 (1999), and references cited therein; (b) T. Onak, J. Jaballas, and M. Barfield, *J. Am. Chem. Soc.*, **121,** 2850 (1999); (c) J. E. Peralta, M. C. Ruiz de Azua, and R. H. Contreras, *Theor. Chem. Acc.*, **105,** 165 (2000).

[13] (a) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *J. Chem. Phys.*, **49,** 2960, 2965 (1968); (b) J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory* (McGraw-Hill, New York, 1970).

[14] *Gaussian 98, Revision A.9*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, USA (1998).

[15] *Gaussian 03, Revision C.02*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford, CT, USA (2004).
[16] A. Bagno, *Chem. Eur. J.*, **6,** 2925 (2000).
[17] (a) D. G. Gorenstein, R. Rowell, and J. Findlay, *J. Am. Chem. Soc*., **102,** 5077 (1980); (b) D. G. Gorenstein, in *Phosphorus-31 NMR: Principles and Applications*; D. G. Gorenstein, Ed. (Academic Press, Orlando, 1984), pp. 37–53.
[18] J. E. Del Bene, S. A. Perera, R. J. Bartlett, J. Elguero, I. Alkorta, C. López-Leonardo, and M. Alajarin, *J. Am. Chem. Soc.*, **124,** 6393 (2002), and references cited therein.
[19] P. Y. Renard, P. Vayron, and C. Mioskowski, *Org. Lett*., **5,** 1661 (2003).
[20] The new, more general relation embracing all discussed *J*-couplings is as follows: $J_{PH}^{\text{total pred}} = 0.9957\, J_{PH}^{\text{FC calcd}} - 0.1383$ ($r^2 = 0.9940, r = 0.9970, SD = 0.29$ Hz, $N = 14$). It was used in Table I. Generally, a good trend is observed.
[21] Z. H. Kudzin and A. Kotyński, *Synthesis*, 1028 (1980).
[22] For the best resolved doublet of this kind found for (*Z*)-**1c**, see Figure 1 in ref.[3]
[23] *PCMODEL V 8.5, Molecular Modeling Software for Windows Operating System, Apple Macintosh OS, Linux and Unix*, Serena Software, Bloomington, IN, USA (2003).
[24] (a) J.-H. Lii and N. L. Allinger, *J. Comp. Chem*., **12,** 186 (1991); (b) M. M. Midland, G. Asirwatham, J. C. Cheng, J. A. Miller, and L. A. Morell, *J. Org. Chem*., **59,** 4438 (1994).
[25] *HyperChem*™ *Release 7.0 for Windows, Molecular Modeling System*, Hypercube, Inc., Waterloo, Ontario, Canada (2002).
[26] D. Jiao, M. Barfield, and V. J. Hruby, *J. Am. Chem. Soc*., **115,** 10883 (1993).
[27] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, and M. J. Frisch, *J. Phys. Chem.,* **98,** 11623 (1994), and references cited therein.
[28] (a) A. L. Spek, *J. Appl. Crystallogr*., **36,** 7 (2003); (b) A. L. Spek, *PLATON: A Multipurpose Crystallographic Tool, Version 230203*, Utrecht University, Utrecht, The Netherlands (2003); http://www.cryst.chem.uu.nl/platon.
[29] A. Bagno, *Chem. Eur. J.*, **7,** 1652 (2001).
[30] http://www.webelements.com.