Theor Chim Acta (1985) 68: 171-178

THEORETICA CHIMICA ACTA

A polarization propagator analysis of the geminal ^{31}P–^{31}P coupling in bis(difluorophosphino)amine*

H. O. Gavarini[1], **M. A. Natiello and R. H. Contreras**[2]

Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria, Pabellón I, 1428 Buenos Aires, Argentina

(Received November 26, 1984)

Inner projections of the polarization propagator (IPPP) are used to decompose in through-space and through-bond contributions the two-bond P-P coupling in PF_2-NH-PF_2. This study is carried out using a ground state INDO wavefunction. Results for a phosphorus *sp* and *spd* atomic basis sets are compared. Several experimental trends are correctly reproduced using either of them. It is concluded that the overlap of the lone pair of both P atoms constitutes a very efficient pathway for transmitting through-space the spin information associated to the Fermi contact term.

Key words: IPPP-INDO — Through-space — P spd basis set — NMR couplings

1. Introduction

In bis(difluorophosphino)amines of type $XN(PF_2)_2$ very large geminal ^{31}P-^{31}P are reported in the current literature for a variety of X substituents. A few examples are as follows: $X = GeH_3$, $^2J_{PP} = 405$ Hz [1]; $X = SiH_3$, $^2J_{PP} = 367.6$ Hz [2]; $X = CH_3$, $^2J_{PP} = 437$ Hz [3, 4], $^2J_{PP} = 442$ Hz [5]; $X = CH_2CH_3$, $^2J_{PP} = 446$ Hz [6]; $X = Ph$, $^2J_{PP} = 382$ Hz [5]. There are several very interesting features of these couplings. For instance, they are strongly dependent on temperature [1, 2], and are notably reduced both upon cation formation [7, 4] and upon complexation with coordination metals [8] and with borane molecules, BH_3 [2].

From an X-ray study it is known that in compound with $X = CH_3$ the lone pairs of both phosphorus atoms overlap [9]. As similar structures can be assumed for

---

* Part of a PhD thesis (H.O.G.) to be presented to the University of Buenos Aires

[1] Fellow of the Argentine National Research Council (CONICET)

[2] Member of the Argentine National Research Council (CONICET)

Offprint requests to: R. H. Contreras

other substituents [2], it was suggested that this lone-pair overlap constitutes an efficient pathway for transmitting the spin information from one P nucleus to the other one [2, 10]. The experimental features quoted above strongly support such an assumption. For instance, the complexation with one molecule of borane is assumed to effectively remove a P lone-pair from the coupling pathway. The influence of two borane molecules can be visualized from a recently reported [11] X-ray study of the bisborane adduct with Ph_2P-NH-PPh_2, where it is found that the BH_3 groups adopt a transoid position, while increasing the P-N-P angle from 118.9° in the uncomplexed diphosphinoamine, to 131.6° in the bisborane adduct.

However, experimental data alone are not enough to evaluate the different factors defining such a behavior. In this sense a theoretical analysis of transmission mechanisms involved in this type of geminal P-P couplings may bring an additional insight on the stereochemical properties of J_{PP} couplings, which could be of great help when using P-P couplings in other compounds as an aid in elucidating conformational preferences. The decomposition of calculated spin-spin coupling constants according to the electronic mechanisms involved in their transmission has received a good deal of attention during the past few years and at present there are several approaches to study this problem [10]. So far, the most versatile method to carry out this type of analysis is the IPPP method [10, 12] (Inner Projections of the Polarization Propagator).

In this paper such an analysis is carried out for the PF_2-NH-PF_2 compound within the INDO approximation. A critical analysis [10] of calculations carried out by Galasso [13, 14] and by Duangthai and Webb [15] indicates that couplings largely dominated by a through-space mechanism where at least a phosphorus lone-pair defines the coupling pathway, requires the use of an *spd* basis set in the INDO approximation. So far the IPPP-INDO method [12], although it was extended to include non-contact terms [16], was only formulated for an sp basis set. For this reason, in this paper the extension of the IPPP-INDO method for analysing spin-spin coupling constants to include an *spd* basis set is also reported. This new version includes the Fermi contact (FC), the spin-orbital (SO) and the spin-dopolar (SD) terms.

2. Theoretical approach

The IPPP formulation was extended to include 3d orbitals for second row atoms. The computational procedure consists in re-writing the IPPP routines to obtain a new version of this program which is adequate to be coupled to the standard CNINDO.3.3.3 program [17]. To develop these modified routines the following points are taken into account. Within the RPA scheme (Random Phase Approximation) the spin-spin coupling constant between nuclei M and N may be written as

$$J^{F}_{M,N} = \Sigma_{ia,jb} \mathbf{V}^{N}_{ia} ({}^{3}\mathbf{A} - {}^{3}\mathbf{B})^{-1}_{ia,jb} \mathbf{V}^{M}_{jb} \tag{1}$$

$$J^{SO}_{M,N} = \sum_{\alpha=1}^{3} \Sigma_{ia,jb} \mathbf{V}^{N\alpha}_{ia} ({}^{1}\mathbf{A} + {}^{1}\mathbf{B})^{-1}_{ia,jb} \mathbf{V}^{M\alpha}_{jb} \tag{2}$$

$$J^{SD}_{M,N} = \sum_{\alpha,\beta=1}^{3} \Sigma_{ia,jb} \boldsymbol{V}^{N\alpha\beta}_{ia} ({}^3\boldsymbol{A} - {}^3\boldsymbol{B})^{-1}_{ia,jb} \boldsymbol{V}^{M\alpha\beta}_{jb} \tag{3}$$

$$J_{M,N} = J^{F}_{M,N} + J^{SO}_{M,N} + J^{SD}_{M,N} \tag{4}$$

where Eqs. (1) to (3), respectively, give the FC, the SO, and the SD terms. The ${}^3\boldsymbol{A}$ and ${}^3\boldsymbol{B}$ matrices are given by

$$({}^3\boldsymbol{A} \pm {}^3\boldsymbol{B})_{ia,jb} = (\varepsilon_a - \varepsilon_i)\delta_{ij}\delta_{ab} - (ab|ji) \pm (aj|bi) \tag{5}$$

Furthermore, assuming that all orbitals are real,

$${}^1\boldsymbol{A} + {}^1\boldsymbol{B} = {}^3\boldsymbol{A} + {}^3\boldsymbol{B}$$

The $\boldsymbol{V}$ arrays contain the matrix elements of the spin Hamiltonian

$$\boldsymbol{V}^{N}_{ia} = \zeta_F \langle i|\delta(\vec{r} - \vec{R}_N)|a\rangle \tag{6}$$

$$\boldsymbol{V}^{N\alpha}_{ia} = \zeta_{SO} \langle i|L^{\alpha}/|\vec{r} - \vec{R}_N|^3|a\rangle \tag{7}$$

$$\boldsymbol{V}^{N\alpha\beta}_{ia} = \zeta_{SD} \langle i|(3|\vec{r} - \vec{R}_N|^2\delta_{\alpha\beta} - (\vec{r} - \vec{R}_N)_{\alpha}(\vec{r} - \vec{R}_N)_{\beta})|\vec{r} - \vec{R}_N|^{-5}|a\rangle \tag{8}$$

where the multiplicative factors ζ involve both the magnetogyric ratios and universal constants.

Within the monocentric approximation for spin-spin couplings [18] all matrix elements in Eqs. (6) to (8) allow a simple expansion where the tensor character of V operators and of the atomic basis orbitals can be used to reduce to a minimum the computational aspects of the problem. The molecular bielectronic integrals of Eq. (5) when expressed in terms of atomic orbitals are notably simplified within the INDO approximation

$$(ij|lm) = \sum_{A,B} \sum_{\mu}^{A} \sum_{\lambda}^{B} C_{\mu i} C_{\mu j} C_{\lambda l} C_{\lambda m} (\mu\mu|\lambda\lambda)$$
$$+ \sum_{A} \sum_{\mu,\nu \neq \mu}^{A} C_{\mu i} C_{\nu j} \{C_{\mu l} C_{\nu m} + C_{\mu m} C_{\nu l}\} (\mu\nu|\mu\nu) \tag{9}$$

where A, B label atoms, and greek indices label atomic orbitals. $C_{\mu i}$ is the coefficient of the ith MO in the μth AO. As part of this work Eqs. (7) to (9) were re-written in order to admit d atomic orbitals. Eq. (6) did not require this extension since within the INDO approach [18] only s atomic orbitals are involved.

When dealing with second row atoms the basic INDO parametrization is not so well defined as for first row atoms and it is known that coupling constants may depend somewhat on the parameter set chosen [13-15, 19]. In this paper the Santry's parametrization of the CNINDO 3.3.3. program is used. Conspicuous differences with the Marsh and Gordon [20] parametrization are observed [10]. Apparently, couplings with important through-space contributions via the P lone pair are more sensitive than other couplings to the parameter set.

Inner projections are performed as explained elsewhere [12]. When using the *sp* basis set the through-space contribution is calculated considering only the subspace defined by the localized molecular orbitals (LMOs) which represent the four antibonding P–F orbitals (vacant LMOs) and the four bonding P–F orbitals, together with all the lone-pairs of the four fluorine atoms and the lone-pairs of both phosphorus atoms (on the whole, eighteen occupied LMOs). Localized molecular orbitals are obtained as explained before [12] where the local atomic basis set is defined by all P and F atomic orbitals. When using the *spd* basis set for the P atoms the selection of the vacant LMOs belonging to the subspace which defines the through-space coupling could not be made on an *a priori* base. The amount of vacant LMOs used in this case was decided choosing those with the norm of its projection in the local subspace close to one. In this way, thirteen vacant LMOs belonging to the projection subspace were found.

Experimental geometrical data were chosen from the X-ray study of the $CH_3N(PF_2)_2$ compound [9] for P–F and P–N interatomic distances as well as for all FPN bond angles. The N–H distance was taken from the standard geometrical model [21]. A planar hybridization was assumed for the N atom, being the same as was experimentally determined for the $CH_3N(PF_2)_2$ compound [9]. Calculations were carried out for different PNP angles, keeping the same symmetry for the whole molecule (vide infra).

3. Results and discussion

The FC term of the $^2J_{PP}$ coupling in PF_2–NH–PF_2 calculated for different PNP angles with a phosphorus *sp* basis set is shown in Fig. 1, together with its through-space (T.S.) and through-bond (T.B.) contributions. Although these two

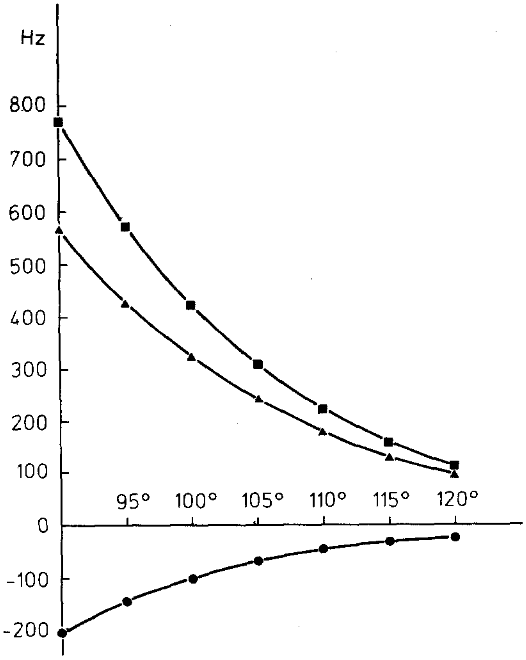

Fig. 1. IPPP-INDO (phosphorus *sp* basis set) analysis of the Fermi contact (FC) term of the two-bond J_{PP} coupling in PF_2–NH–PF_2 for different values of the PNP angle. (▲): Total FC contribution; (■): Through-space component (T.S.); and (●): Through-bond component obtained subtracting from the total FC contribution that of the through-space component

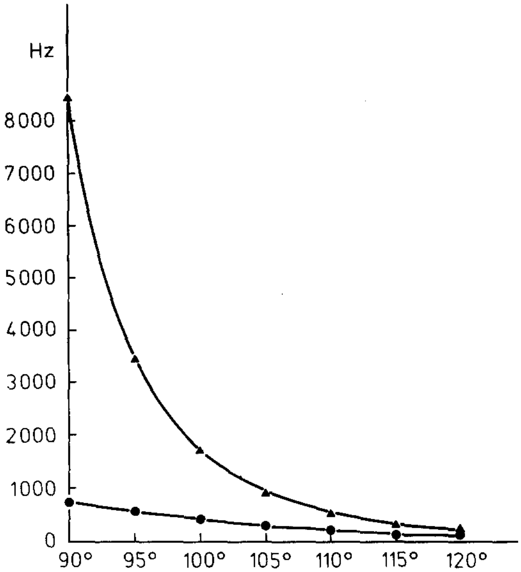

Fig. 2. IPPP-INDO through-space components of the Fermi contact term of the two-bond J_{PP} coupling in PF_2-NH-PF_2 for different values of the PNP angle. (▲): values obtained using a phosphorus *spd* basis set; (●): values obtained using a phosphorus *sp* basis set (cf. Fig. 1)

contributions strongly depend on the bond PNP angle, the T.S. one increases more rapidly when decreasing this angle. Both contributions are of opposite sign. Non-contact contributions are by far much smaller, being negligible in comparison with the Fermi term. When using a phosphorus *spd* basis set, trends are quite similar, although they are all magnified. A comparison of the FC T.S. contribution calculated using both *sp* and *spd* phosphorus basis sets is shown in Fig. 2. It must be recalled that the first one, i.e., the FC T.S. contribution using a P *sp* basis set, is the same as that shown in Fig. 1 (■), although it is shown now using a different scale.

In Table 1 the T.S. and T.B. contributions to the FC, SO and SD terms are shown for a PNP angle of 115°. This angle is close to the X-ray experimental one in PF_2-NH_3-PF_2, 116° [9]. For this angle the total coupling, calculated either with the *sp* or *spd* phosphorus basis set, is somewhat smaller than the experimental values quoted in the Introduction for different substituents. However, as it is shown in Fig. 2, the calculated value increases so much with the PNP angle for the *spd* basis set, that a slightly smaller assumed PNP angle in the fluid state can easily account for the observed coupling constant. It is also interesting to observe that a through-space component of the orbital term of −9.19 Hz is obtained with the IPPP-INDO/*spd* calculation. Although it is much smaller than the corresponding FC term, a non-contact through-space contribution as large as that has not been calculated so far ([16] and references cited therein). It is interesting to observe that the experimental trends known for this type of couplings are well accounted for with the behavior obtained for the Fermi contact term. In fact, the strong dependence with the temperature [1, 2] is in agreement with the strong dependence on the PNP angle. The large reduction in the absolute value of this coupling after complexation with a BH_3 (2) molecule can be explained by an

Table 1. Different contributions to the $^2J_{PP}$ coupling in PF_2-NH-PF_2 molecule for a PNP angle of 115°[a,b]

		Total	T.S.	T.B.
FC	*sp*[c]	134.05	162.32	−28.27
	spd[d]	182.73	347.72	−164.99
SO	*sp*[c]	−0.15	0.23	−0.38
	spd[c]	−3.56	−9.19	−5.63
SD	*sp*[c]	0.37	0.02	0.35
	spd[d]	−1.54	−0.37	−1.17

[a] The experimental X-ray PNP angle in PF_2-NCH_3-PF_2 is 116° [9]

[b] All values are in Hz

[c] Values calculated using a phosphorus *sp* basis set

[d] Values calculated using a phosphorus *spd* basis set

inhibition of the through-space mechanism together with a larger PNP angle, which would reduce the absolute value of the T.B. contribution. This result is in line with previously reported calculations [10] where the successive elimination of both phosphorus lone pairs from the coupling path yielded a systematic decreasing of the P-P coupling.

The drastic reduction in the $^2J_{PP}$ coupling upon complexation with two BH_3 molecules [2] can be explained considering that in $Ph_2P(BH_3)$-NH-$PPh_2(BH_3)$ a transoid arrangement is taken by the BH_3 molecules and the PNP angle is increased in about 12.7° [11]. This transoid arrangement prevents a through-space transmission of the spin information, while the increase in the PNP angle greatly reduces the absolute value of the T.B. contribution.

Another point worth commenting on is the following. In the solid state an overlap of both P lone-pairs has been determined experimentally in PF_2-NCH_3-PF_2. According to the present analysis the through-space component is large and positive. The experimental determination of this coupling in solution also yields a positive value, which according to the present work, is opposite in sign to the T.B. component. This constitutes an evidence that in the fluid state both P lone-pairs also overlap, and that they constitute a very efficient pathway for transmitting the spin information. In order to establish how far the INDO approximation describes this overlap, the degree of bonding, according to Armstrong et al. [22], has been calculated for a phosphorus *sp* basis set, obtaining a value of 0.0156. This value, although small, is conspicuously larger than the usual degree of bonding between "classically" (i.e. according to chemical intuition) non-bonded atoms.

For a PNP angle smaller than 105° the ground state INDO wave function becomes "quasi-unstable" non-singlet Hartree-Fock when the phosphorus *spd* basis set is used. As discussed previously, in that case the calculation of both the Fermi contact term as well as the spin-dipolar becomes meaningless [23]. However, localized molecular orbitals defining the subspace where the T.S. component is calculated (vide supra) do not contribute to this "quasi-instability". For this reason they were calculated as shown in Fig. 2, even for a PNP angle as small as 90°.

4. Conclusions

Although the theoretical estimate of the through-space component of the P-P coupling under study depends rather strongly both on the INDO parameters set chosen for second row atoms and on the atomic orbitals basis set for the P atom, several features were found which do not depend on them. For instance, this P–P coupling is largely dominated by a positive through-space component of the Fermi contact term. This indicates that the overlap of phosphorus non-bonding electron pairs constitutes a very efficient pathway for transmitting the spin information associated with the FC term. Non-contact contributions are by far much smaller, be they transmitted "through-bond" or "through-space".

The decreasing absolute value of the T.B. component with increasing the PNP angle and the influence of the overlapping of the P lone-pairs in the total coupling by means of the T.S. component are consistent with the trends arising from experimental results.

The possibility of using J_{PX} couplings ($X = {}^1H, {}^{13}C$) in a stereochemical analysis is at present very well known and several aspects of it were discussed in a previous paper [10]. The large T.S. contribution to P–P couplings with proximate lone-pairs indicates that this last type of coupling may be a powerful tool for elucidating preferential conformations.

A point which so far is not so well understood is if the overlap of phosphorus non-bonding electron pairs yields a stabilizing effect, or, on the contrary, whether there is a repulsion energy between them, and they can only overlap when there are other effects such as steric interactions which force the proximity of lone-pairs. A study of this problem is at present in progress in this laboratory.

Acknowledgments. Grants from the Argentine National Research Council (CONICET) and from the Argentine Science and Technology Secretariat (SECYT) are gratefully asknowledged. The authors thank the authorities of SEYCAD (Data Processing Center of the Argentine Navy) for providing computational time.

References

1. Ebsworth, E. A. V., Rankin, D. W. H., Wright, J. G.: J. Chem. Soc. Dalton Trans. 2348 (1977)
2. Ebsworth, E. A. V., Rankin, D. W. H., Wright, J. G.: J. Chem. Soc. Dalton Trans, 1065 (1979)
3. Nixon, J. F.: J. Chem. Soc. (A) 2689 (1968)
4. Light, R. W., Paine, R. T., Maier, D. E.: Inorg. Chem. **18**, 2345 (1979)
5. King, R. B., Lee, T. W.: Inorg. Chem. **21**, 319 (1982)
6. Johnson, T. R., Nixon, J. F.: J. Chem. Soc. (A) 2518 (1969)
7. Nixon, J. F.: Chem. Commun. 669 (1969)

8. Newton, M. G., King, R. B., Chang, M., Gimeno, J.: J. Am. Chem. Soc. **99**, 2802 (1977)
9. Hedberg, E., Hedberg, L., Hedberg, K.: J. Am. Chem. Soc. **96**, 4417 (1974).
10. Contreras, R. H., Natiello, M. A., Scuseria, G. E. In: Magnetic Resonance Review, Vol. 9, p. 239. Poole, C. P., Jr. (ed.) London: Gordon and Breach 1985
11. Nöth, H., Fluck, E.: Naturforsch. **39b**, 744 (1984)
12. Engelmann, A. R., Contreras, R. H.: Int. J. Quantum Chem. **23**, 1033 (1983)
13. Galasso, V.: J. Magn. Reson. **34**, 199 (1979)
14. Galasso, V.: J. Magn. Reson. **36**, 181 (1979)
15. Duangthai, S., Webb, G. A.: Org. Magn. Reson. **21**, 199 (1983)
16. Natiello, M. A., Scuseria, G. E., Contreras, R. H.: Chem. Phys. Lett. **108**, 589 (1984)
17. Beer, M. D.: Daresbury Laboratory, NMR Program Library
18. Pople, J. A., Beveridge, D. L.: Approximate Molecular Orbital Theory, New York: McGraw-Hill. 1970
19. Beer, M. D., Grinter, R.: J. Magn. Reson. **26**, 421 (1977)
20. Marsh, F. J., Gordon, M. S.: J. Mol. Struct. **31**, 345 (1976)
21. Pople, J. A., Gordon, M.: J. Am. Chem. Soc. **89**, 4253 (1967)
22. Armstrong, D. R., Perkins, P. G., Stewart, J. J. P.: J. Chem. Soc. Dalton Trans. 838 (1973)
23. Scuseria, G. E., Contreras, R. H.: Theoret. Chim. Acta (Berl.) **59**, 437 (1981); Scuseria, G. E., Engelmann, A. R., Contreras, R. H.: Theoret. Chim. Acta (Berl.) **61**, 49 (1982)