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Supporting Information

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SUPPORTING INFORMATION

First example of a discrete P··I—I··P assembly. The large influence of weak interactions on the ^{31}P-NMR of iodinated phosphorus compounds.

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Experimental Section

2: I_2 (11 mg, $4.4 \cdot 10^{-2}$ mmol) was added to a solution of **1** (15 mg, $4.4 \cdot 10^{-2}$ mmol) in CH_2Cl_2 (5.0 ml). The solution was stirred at room temperature for 1 h and left for two months at +4 ºC. After this time red brown crystals were obtained. Yield: (18 mg, 85 %). ^{1}H-NMR (300.13 MHz, $CDCl_3$, 25 ºC, TMS): δ= 2.23 (s, 3 H, CH_3), 7.45-7.89 (m, 10 H, C_6H_5); ^{11}B-NMR (96.29 MHz, $CDCl_3$, 25 ºC, $Et_2O \cdot BF_3$): δ= -0.3 (d, ^{1}J(B,H)= 145 Hz; 1 B), -4.6 (d, ^{1}J(B,H)= 149 Hz, 1 B), -8.8 (d, ^{1}J(B,H)= 150 Hz, 8 B); ^{31}P{^{1}H}-NMR (121.48 MHz, $CDCl_3$, 85% H_3PO_4): 25 ºC, δ= 6.0 (s). Elemental analysis for $C_{30}H_{46}B_{20}I_2P_2$: calc: C 38.39, H 4.91; found C 38.65, H 5.01.

Crystal Data: The X-ray diffraction data were collected at 294 K with a Rigaku AFC-5S four-circle diffractometer using graphite -monochromated $Mo_{K\alpha}$ radiation (λ = 0.71069 Å). Crystal data for **2**: Formula $C_{30}H_{46}B_{20}I_2P_2$, M_r = 938.61, crystal size: 0.20 x 0.12 x 0.10 mm, monoclinic, space group $P2_1/n$ (No. 14), a = 8.0101(19), b = 9.398(3), c = 28.453(3), β = 94.09(2)º, V = 2136.4(9) Å^3, Z = 2, D_{calc} = 1.459 g cm^{-3}, μ = 1.571 mm^{-1}, F(000) = 924 , Reflections collected 4319, unique 3752 [R(int) = 0.0393]. An empirical absorption correction with ψ-scan data was applied. The structure was solved using SIR92 and was refined against $|F^2|$ using program SHELXL-97 (244 parameters). R indices were ($I > 2\sigma(I)$): R1 = 0.050, wR2 = 0.099.

Study of δ ^{31}P NMR and molar conductivity for different **1**:I_2 ratios with the temperature.

In Figure 1 plots of δ ^{31}P NMR (DCM) vs. *T* for the different **1**:I_2 ratios studied are represented. It is very significant the similarity of the traces for ratios of I_2 equal or superior to 0.5. This supports that the **1**·I_2·**1** species is the one present in solution, and that excess of I_2 does not interfere much in the ^{31}P-NMR. The more negative δ value observed has been around -23.0 ppm in DCM at 175 K, but this is for technical reasons due to freezing of the solvent. Molar conductivity measurements Λ were done for 1:0.5 and 1:1 ratios in DCM at 301, 243 and 203 ºK, [**1**]= 3 x 10^{-2} M to rule out that ionic species were generated in these low temperature studies. In all cases Λ were very low in the range of 1/20 to 1/40 of the Λ value for tetrabuthylammonium chloride at 3 x 10^{-2} M.

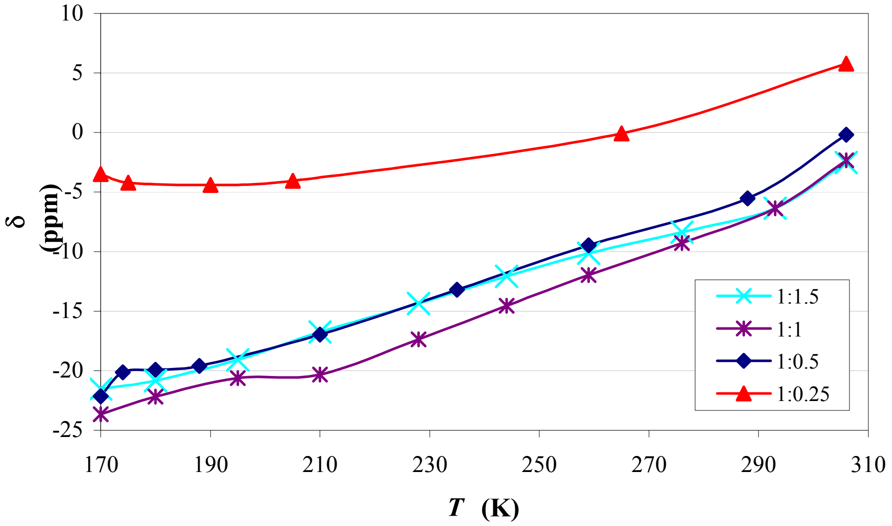

Figure 1. Influence of the temperature on the ^{31}P-NMR in solutions with different **1**:I_2 ratios; 1:0.25, 1:0.5, 1:1 and 1:1.5.

Computational Details

All calculations have been carried out with the Gaussian-98 package[1] using either the 6-31+G* or 6-311+G** basis[2] sets for all atoms except iodine, at the B3LYP computational level.[3,4] For I, the 6-311G* basis set was used.[5] The geometry of all molecules has been taken from crystal structure data. The absolute isotropic chemical shieldings have been calculated for all structures with the GIAO method[6] at the same computational level mentioned before. For relative isotropic chemical shieldings, triphenylphosphane parameters from X-ray data have been used for the calculations.[7]

Attempts to reproduce the geometrical parameters of $Ph_3P{\cdot}I_2$

Geometry optimizations on $Ph_3P{\cdot}I_2$ have been done with different basis sets in order to reproduce geometric distances. In all cases, basis set 6-31G* has been used for C and H, and basis sets for P and I are shown in Table 1. In the latter, a comparison between experimental and calculated distances is shown. As seen from Table 1, no distances matching between computed and experimental structure has been observed.

	Basis set			
	lanl2dz for P and I	**lanl2dz (d,p) for P and I**	**6-311G* for I, 6-31G* for P**	**Experimental**
d(P-I)	2,781	2,749	2,808	2,481
d(I-I)	3,082	2,954	2,945	3,160

Table 1. Comparison between experimental and calculated distances

Influence of P···I(1)···I(2) distances on the ^{31}P-NMR

Crystal structure data has been used for all NMR calculations.[7] In order to correlate the P··I(1)··I(2) parameters and their chemical shift, two sets of calculations have been done altering the P··I(1) and I(1)··I(2) distances. These calculations have been done using GIAO B3LYP/6-31+G* for all atoms except for iodine, for which the 6-311G* basis set was used. Conclusions are indicated in the text, and computed δ values are shown in Figures 2 and 3.

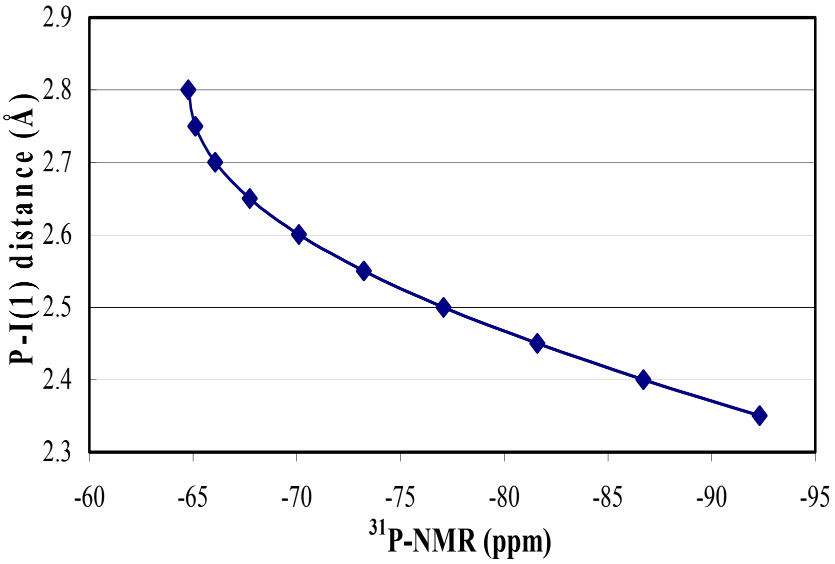

Figure 2. Influence of P-I(1) distance on the ^{31}P-NMR in P··I(1)··I(2), while maintaining P··I(2) constant at 5.64 Å.[7]

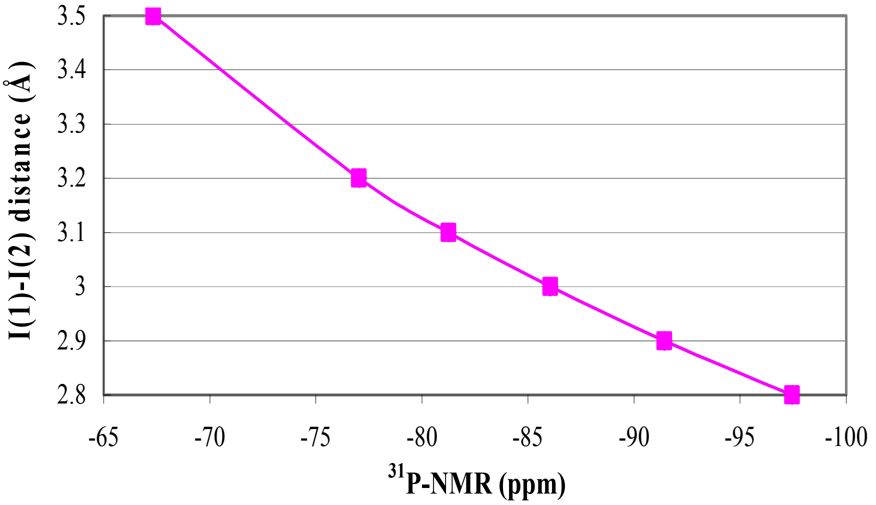

Figure 3. Influence of I(1)-I(2) distance on the ^{31}P-NMR in P··I(1)··I(2), while maintaining P··I(1) constant at 2.481 Å.[7]

Calculation of ^{31}P-NMR for $Ph_3P{\cdot}I_2$ and $[Ph_3PI]^+$

^{31}P-NMR calculated chemical shifts of $Ph_3P{\cdot}I_2$, $[Ph_3PI]^+$ and $[Ph_3IPI]^+[I_3]^-$ using GIAO B3LYP/6-311+G** for C, H and P and B3LYP/6-311G* for I are shown in Table 2:

	calculated ^{31}P-NMR	Experimental
$Ph_3P{\cdot}I_2$	-26.29	-23,4[6]
$[Ph_3PI]^+$	-282.37	44,8[7]
$[Ph_3PI]^+I_3^-$	36.36	44,8[7]

Table 2. ^{31}P-NMR calculated chemical shifts

Butadiene model for the shortening of the I···I distance.

A σ-only molecular scheme identical to the one reported[8c] for the S··I-I··S array of atoms accounting for the lengthening of the S··I bonds and the shortening of the I-I distances, would also apply to the results reported here. If only the participating σ orbitals are considered in the X-I··I-X motif, a 1,3-

butadiene energy diagram such as this shown in Figure 4 would be observed. There are 6 electrons to be arranged in this system, two from each donor and two from σ in the I_2 fragment. Orbitals σ_1 and σ_2 are bonding while σ_3 is antibonding. The latter has, however, a bonding interaction between I and I while shows antibonding interactions between both P/I entities. This explains the shorter I-I distance in the I_2 bridging motifs.

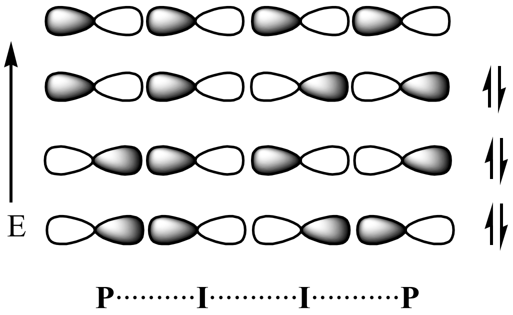

Figure 4. 1,3-Butadiene energy diagram.

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[5] Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 02/25/04, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. Contact Karen Schuchardt for further information.

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