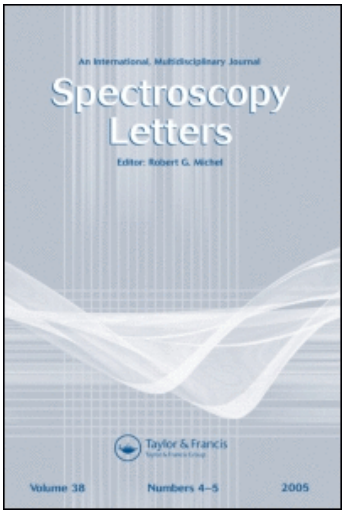

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Longitudinal Relaxation of the Quaternary Carbons of Some Phosphine Oxides

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LONGITUDINAL RELAXATION OF THE QUATERNARY CARBONS OF SOME PHOSPHINE OXIDES.

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ABSTRACT

A detailed analysis of the longitudinal relaxation of the quaternary carbons of the phenyl groups in some diphenylphosphine oxides, and a comparison of the NMR data with X-Ray and theoretical results show that Cq(1) (cf. figure 1) relaxes mainly through an intramolecular DD mechanism and that dipolar interactions with atoms more than 3.5 A away are unimportant. Residual mechanisms play a major role in the relaxation of Cq(2) and they are identified as CSA and/or SR mechanisms.

INTRODUCTION

X-ray, NMR and molecular mechanics studies on five different diphenylphosphine oxides, $(Ph)_2POx$ (Figure 1), were recently carried out [1-4]. They allowed a clear characterization of the structural, conformational and dynamical properties of these compounds. In the course of these investigations the longitudinal relaxations of the quaternary carbons of the phenyl groups di-

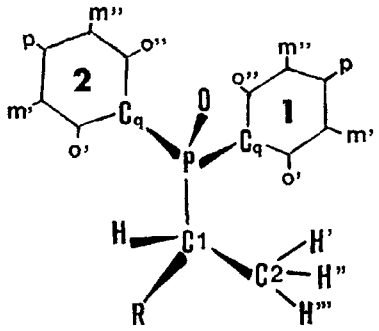

Figure 1. The main molecular frame of the considered diphenylphosphine oxides. The R substituent has the following form for the different compounds:

R = OCH_2CH_2Ph	compound 9
R = OCH_3	" 10
R = $OCH_2CH_2CH(CH_3)_2$	" 11
R = $OCH_2(CH_2)_{10}CH_3$	" 12

rectly attached to the phosphorus atom were not considered in detail. Now, a closer analysis of the mass of collected spectroscopic and theoretical data has given us a deeper insight of the longitudinal relaxation of these quaternary carbons.

EXPERIMENTAL

T_1 data of phosphine oxides in $CDCl_3$ solutions (0.3 M) at 50 MHz were obtained as explained in ref. 3. Accurate X-ray geometries are given in ref. 1, while the results of molecular mechanics calculations are reported in ref. 2.

RESULTS AND DISCUSSION

The longitudinal relaxation times of the quaternary carbons Cq(1) and Cq(2) of Ph(1) and Ph(2) respectively, are collected in

TABLE 1: Longitudinal relaxation values of the quaternary Phenyl carbons of compounds 9 through 12.

Compounds:		9	10	11	12
T_1(Cq(1))	s	17.8	24.3	18.3	14.1
T_1(Cq(2))	"	18.6	25.3	19.2	15.6

TABLE 2: τ_{eff} values of Ph(1), Ph(2) and C2-Me groups and τ_R values of compounds 9 through 12

Compound :		9	10	11	12
$\tau_{eff}(1)/10^{-11}$	s	3.18	2.02	2.9	4.08
$\tau_{eff}(2)$/	" "	2.04	1.47	1.72	2.22
τ_{eff}(Me)/	" "	1.37	1.07	1.29	1.63
τ_R /	" "	4.3	3.2	4.1	5.6

table 1. The effective correlation times of Ph(1,2) and C2-Me and the rotational correlation times of the overall $(Ph)_2PO_x$ molecule [3] are listed in table 2. The geometrical data from the crystal structures [1] of phosphine oxides 9,10 and 11 and from the theoretical calculations on the non-crystalline compound 12 [2], are reported in table 3, where the distances between the Cq atoms

TABLE 3: Distances (in Å) between the quaternary carbons of the Ph groups and the nearest protons and P atoms of compounds 9 through 12.

Distances/Compound:	9	10	11	12
Cq(1)-Ho'(1)	2.047	2.086	2.010	2.180
Cq(1)-Ho''(1)	2.010	2.044	2.070	2.182
Cq(1)-Hm'(1)	3.283	3.292	3.220	3.428
Cq(1)-Hm''(1)	3.281	3.272	3.272	3.428
Cq(1)-Hp(1)	3.727	3.757	3.736	3.914
Cq(1)-Ho'(2)	3.546	4.464	3.837	4.650
Cq(1)-Ho''(2)	3.948	2.713	3.551	2.753
Cq(2)-Ho'(2)	2.084	2.024	2.032	2.179
Cq(2)-Ho''(2)	2.032	2.055	2.049	2.181
Cq(2)-Hm'(2)	3.248	3.280	3.235	3.428
Cq(2)-Hm''(2)	3.278	3.292	3.282	3.426
Cq(2)-Hp(2)	3.746	3.756	3.744	3.917
Cq(2)-Ho'(1)	3.132	3.435	4.221	3.317
Cq(2)-Ho''(1)	4.157	4.013	3.105	4.263
Cq(1)-H1	3.766	3.723	2.976	3.090
Cq(2)-H1	2.960	3.008	3.030	3.060
Cq(1)-H2'	4.425	4.239	4.289	4.397
Cq(1)-H2''	3.064	2.887	3.031	2.961
Cq(1)-H2'''	3.812	3.505	3.615	3.898
Cq(1)-P	1.804	1.810	1.805	1.816
Cq(2)-P	1.805	1.804	1.806	1.816
Cq(2)-Hm'(1)	4.157			

TABLE 4: Calculated dipole-dipole relaxation rates and relaxation times of the Cq atoms of Ph(1) and Ph(2) of compounds 9 through 12.

Compound:		9	10	11	12
$R_{1DD}(1)/10^{-3}$	s^{-1}	44.7	35.0	42.0	44.3
$T_{1DD}(1)$	s	22.4	28.6	23.8	22.0
$R_{1DD}(2)/10^{-3}$	s^{-1}	32.7	23.8	29.2	29.7
$T_{1DD}(2)$	s	30.6	42.0	34.3	33.7

and all other atoms less than 4.4 A away are listed. The resulting calculated longitudinal relaxation rates and times of Cq(1) and Cq(2) due to the intramolecular dipolar interactions of Cq with the neighboring protons and phosphorus atoms are given in table 4. They have been calculated by the aid of the equation [5,3]

$$R_{1DD} = K^2 \Sigma(1/r)^6 \tau_c \qquad (1)$$

where $K = (\mu_o/4\pi)\hbar \gamma_C \gamma_I$ with I=H or P, r=distance between Cq and H or P (in m) and $\tau_c = \tau_R$ or τ_{eff} for the Cq--H(Ph)/H(C2) interactions [1]. The sum in (1), for each Cq, is over all distances given in table 3.

The $(Ph)_2POx$ groups show a trans conformation along the P-C1 bond, with Ph(1) gauche to C2-Me, while the side-chain R, at its end, folds back towards Ph(1) [1-4]. Table 5, in which the contributions of the different dipolar interactions are collected, shows that the largest contributions are due to the Cq--Hortho

TABLE 5: Percent (%) contribution of the different relaxation paths to the calculated overall dipolar relaxation rate of Cq(1 and 2) of compounds 9 through 12.

Paths / Compound:	9	10	11	12
Cq(1)--H*ortho*(1)	73.8	65.9	69.4	61.7
Cq(2)--H*ortho*(2)	59.4	62.0	58.9	50.3
Cq(1)--H*meta*(1)	4.1	4.1	4.3	4.1
Cq(2)--H*meta*(2)	3.7	3.5	3.6	3.3
Cq(1)--H*para*(1)	1.3	1.4	1.3	1.3
Cq(2)--H*para*(2)	1.7	1.7	1.8	1.9
Cq(1)--H*ortho*(2)	1.3	4.9	1.2	4.3
Cq(2)--H*ortho*(1)	4.4	2.6	4.6	4.6
Cq(2)--H*meta'*(1)	0.7	-	-	-
Cq(1)--P	16.5	18.9	16.7	20.9
Cq(2)--P	22.5	23.1	24.0	31.2
Cq(1)--H1	1.2	1.5	5.1	5.2
Cq(2)--H1	7.0	6.5	6.6	8.3
Cq(1)--H2	1.8	3.3	2.1	2.5
Cq(2)--H2	0.4	0.5	0.5	0.5

The Cq--*ortho/meta* path includes the two *ortho/meta* protons and the Cq--H2 path includes the three methyl protons.

Cq(2)--H2 distances are between 4.4 and 5.2 Å.

interactions, followed by the Cq--P interactions, and then by the Cq(2)--H1 interaction. Cq(1)--H1 in 11 and 12, as well as most Cq(1)--Hortho(J) and Cq--Hmeta interactions are around 4-5%, while the interactions of Cq with hydrogen atoms more than 3.5 A away are unimportant.

Table 4 deserves a deeper attention. Comparison with table 1 shows that the experimental and calculated relaxation times for Cq(1) are in a good agreement (a T_1 error around 20% for slowly relaxing carbons may be accepted), while those for Cq(2) differ considerably. It can then be inferred that intramolecular dipolar interactions are the main relaxation mechanism for Cq(1), and that a residual mechanism is playing an important role for Cq(2). The residual relaxation for Cq(2) ($R_{1r}=R_{1DDexp} - R_{1DDcalc}$) is

compound:	9	10	11	12
$R_{1r}(2)/10^{-3}$ s^{-1}	21.1	15.7	22.9	34.4

The origin of this residual relaxation could be:

a) a contribution from an intermolecular heteronuclear dipole-dipole mechanism, $R_{1DD}(inter)$, i.e., an interaction with the solvent;

b) a contribution from a chemical shift anisotropy mechanism, R_{1CSA};

c) a contribution from a spin-rotation mechanism, R_{1SR};

d) a combination of these mechanisms, more active on Cq(2) than on Cq(1).

The particular conformation of the considered phosphine oxides, with Ph(1), C2-Me and the R groups forming a kind of molecular pocket [4], would make the interactions of Cq(1) with the solvent quite difficult. On the other hand, with this particular conformation, the charge distribution (i.e. the anisotropy term)

around Cq(1) may be different than that around Cq(2), while strong steric effects on Ph(1) [4] could lessen to a good extent the spin-rotation mechanism on Cq(1). If we assume that the residual mechanism active on Cq(1) is nearly half of that acting on Cq(2), i.e.:

compound	9	10	11	12
$R_{1r}(1)/10^{-3}$ s^{-1}	10.5	7.9	11.5	17.2

and add this residual to the calculated DD mechanism, the corresponding total T_{1T} become

compound	9	10	11	12
$T_{1T}(1)$ s	18.1	27.4	18.7	16.2

The agreement between these and the experimental Cq(1) relaxation values (table 1) is now good.

When a Brownian diffusion through a homogeneous viscous medium is assumed, the inter-hetero DD relaxation of Cq by a spin nucleus I can be calculated, using the relation [5]

$$R_{1DD}(\text{inter}) = K^2 \ (2\ N_I \ / \ 15\ D\ a) \qquad (2)$$

where N_I=number density of spin I in solution, D=mutual translational self-diffusion coefficient of solute and solvent molecules, a=length of closest approach of Cq and I. The diffusion coefficient is estimated by the Stokes-Einstein relation:

$$D = k\ T\ /\ 6\ \eta\ r \qquad (3)$$

with η =.52 cP, T=303°K and r=4.3 Å [4], then D≈10^{-5} $cm^2 s^{-1}$. In 99.9% $CDCl_3$ N_H is too small and dipolar contributions from D and Cl become important; then, eq 2, with $N_I \approx 10^{22}$ (I=D or Cl) and a=1.5 Å (average between C-D and C-Cl bond lengths), gives the

intermolecular component as $R_{1DD}(inter) \approx 1.7\ 10^{-5}\ s^{-1}$. This value, even if approximate, is too small (by three orders of magnitude) to account for the residual relaxation value of $(Ph)_2POx$.

On the other hand it has been found [6] that for the non-protonated C-1 carbon of toluene, at 63 MHz, approximately 10% of the relaxation is due to the CSA mechanism and around 50% to the SR mechanism, while for the non-protonated acetylenic carbons of diphenyldiacetylene (DPDA), at 63 MHz, around 90% of the relaxation is due to the CSA mechanism. Wilkie [7] also reported that the SR mechanism becomes important at room and high temperatures for the carbon atoms of many phenylphosphorus compounds, Ph-P.

A direct comparison between the data for the asymmetric $(Ph)_2POx$ molecules and those for the more symmetric toluene, DPDA and Ph-P molecules, measured under different experimental conditions, is not straightforward. Nevertheless even a cautious use of these results would suggest that for the considered phosphine oxides the SR and/or CSA mechanisms are active on the relaxation of Cq(2) and, in a minor way, of Cq(1).

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