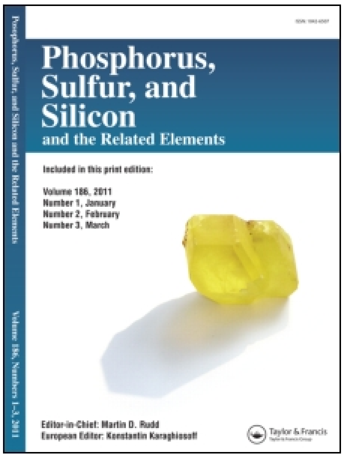

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SOLID STATE CONFORMATION AND ^{31}P CP/MAS NMR STUDIES OF (5,5-DIMETHYL-1,3-DITHIAN-2-YL)TRIPHENYL-PHOSPHONIUM CHLORIDE AND (5,5-DIMETHYL-1,3-DITHIAN-2-YL)TRIMETHYL-PHOSPHONIUM CHLORIDE

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SOLID STATE CONFORMATION AND ^{31}P CP/MAS NMR STUDIES OF (5,5-DIMETHYL-1,3-DITHIAN-2-YL)TRIPHENYL-PHOSPHONIUM CHLORIDE AND (5,5-DIMETHYL-1,3-DITHIAN-2-YL)TRIMETHYL-PHOSPHONIUM CHLORIDE

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Dedicated to Professor Reinhard Schmutzler on the occasion of his 60th birthday

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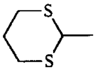
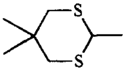
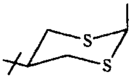
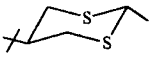
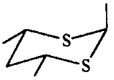
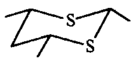
The crystal structures of the title compounds, 5,5-dimethyl-2-triphenylphosphonio-1,3-dithiane **1b** and 5,5-dimethyl-2-trimethylphosphonio-1,3-dithiane **4b**, have been determined by X-ray methods. Structure solution by direct methods and refinement by least-squares gave R = 0.044 and 0.046, respectively. The 1,3-dithiane ring in **1b** adopts a chair conformation with the triphenylphosphonium group being axial while in **4b** the trimethylphosphonium group is equatorial. Comparison of bond distances in **1b** and **4b** suggests that the n_S-σ^*_{C-P} negative hyperconjugation may be responsible for the anomeric effect operating in the S—C—P$^+$ system. The ^{31}P CP/MAS NMR spectra of both title compounds were recorded and discussed.

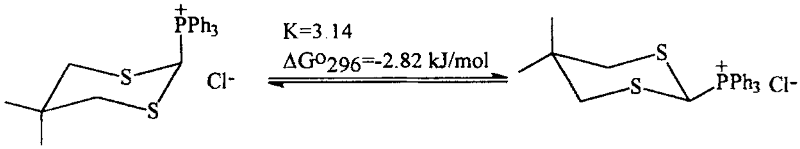
Key words: Conformation, anomeric effect, X-ray diffraction, 2-phosphonio-1,3-dithianes, ^{31}P CP/MAS NMR spectra.

INTRODUCTION

In the course of our studies on the anomeric effect in 1,3-diheteroanes[1] we became interested in the conformation of 1,3-dithianes bearing phosphonium substituents at the anomeric carbon atom. The main reason to investigate conformational behaviour of this class of compounds was that the anomeric interactions in the S—C—P$^+$ fragment are at least formally similar to those in the O—C—N$^+$ systems which exhibit a so-called reverse anomeric effect, i.e., the equatorial preference of the ammonium substituents.[2–4] It was expected that the latter effect may also be operative in the S—C—P$^+$ system, if the electrostatic explanation is correct. Having this in mind, a large number of 2-phosphonio-1,3-dithianes **1–4** shown as follows was prepared and investigated.[5–7]

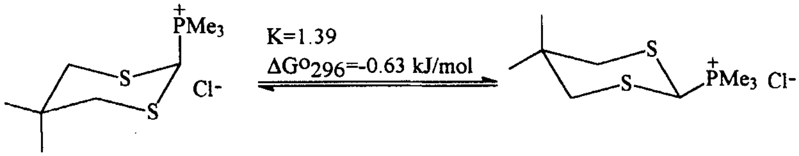
Ring	$\overset{+}{P}Ph_3$	$\overset{+}{P}Ph_2Me$	$\overset{+}{P}PhMe_2$	$\overset{+}{P}Me_3$
	**1a**	**2a**	**3a**	**4a**
	**1b**	**2b**	**3b**	**4b**
	**1c**	**2c**	**3c**	**4c**
	**1d**	**2d**	**3d**	**4d**
	**1e**	**2e**	**3e**	**4e**
	**1f**	**2f**	**3f**	**4f**

Both equilibration of diastereomeric 2-phosphonio-1,3-dithianes and NMR studies on conformationally labile models revealed the operation of the generalized anomeric effect.[7,8] Thus, for 2-phosphonio-1,3-dithianes **3a–f** and **2c–d** the axial preference ($K < 1$, $\Delta G^0 > 0$) was found to predominate. In other cases only a slight equatorial preference was observed that was interpreted in terms of the competition between the anomeric effect and the steric effect involving repulsive 1,3-syn-diaxial interactions. For example, for the conformational equilibria of 2-phosphonio-1,3-dithianes **1b** and **4b** (Equations 1 and 2) the K and ΔG^0_{296} values were calculated using the Eliel equation with the assumption that the value of the γ-effect on ^{13}C-NMR chemical shift is the weighted average value of those for the model diastereomeric dithianes **1c–d** and **4c–d**, respectively.



(eq.1)

1b-ax **1b-eq**



(eq.2)

4b-ax **4b-eq**

However, in spite of the fact that in both dithianes shown above the equatorial preference predominates ($K > 1$, $\Delta G^0 < 0$), the values of the anomeric effect, ΔG^0_{AE}, calculated according to Franck's methodology are quite large and equal to 8.5 and 9.5 kJ/mol for **1b** and **4b**, respectively. This prompted us to study their solid state conformations by X-ray analysis which revealed that **1b** exists in the crystal in a chair conformation with the Ph_3P^+ group being axial while in **4b** the Me_3P^+ group is equatorial.

RESULTS

Crystal and Molecular Structure of 1b

A three-dimensional view of 2-triphenylphosphonio-1,3-dithiane **1b** with the atom numbering is shown in Figure 1. Figure 2 shows the Newman projection around the C(1)—P bond together with the relevant torsional angles. The crystal packing of **1b** in the unit cell is presented in Figure 3. In Table I the crystal data of **1b** are collected. Positional coordinates are in Table II. Table III and IV contain inter-atomic distances and bond angles. Table V contains torsional angles.

An inspection of Figure 1 clearly reveals that the six-membered dithiane ring in **1b** adopts a chair conformation [$\Delta C_S^{(C1)} = 1.6(2)$] with the axial C(1)—P bond. The angle between this bond and the basic S(1), S(2), C(2), C(4) plane was found to be 82.6°. In order to estimate the deviations of the dithiane ring in **1b** from ideal chair conformation, the angles between the above mentioned plane and the plane containing C(1), S(2) and S(4) atoms and the plane formed by C(2), C(3) and C(4)

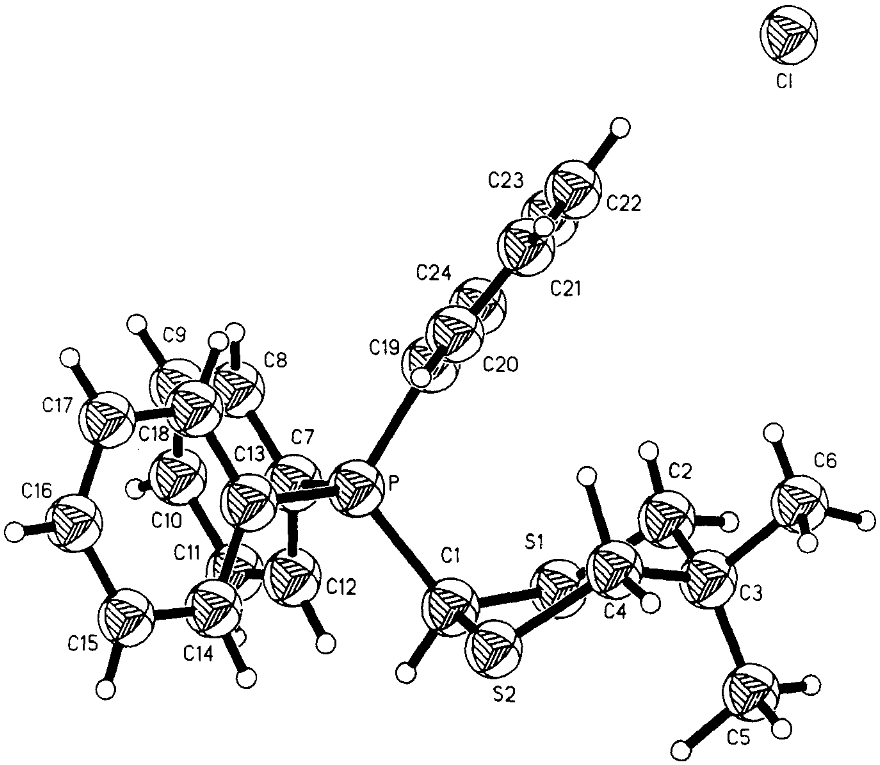


FIGURE 1 The solid state conformation (ORTEP) of the dithiane **1b**, with atom numbering system.

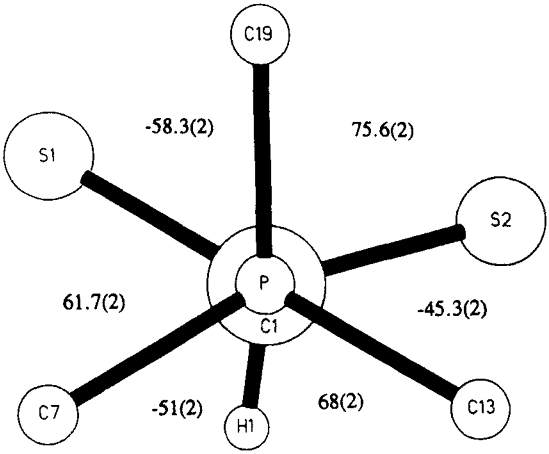


FIGURE 2 The Newman projection around the C(1)—P bond and the relevant torsion angles in **1b**.

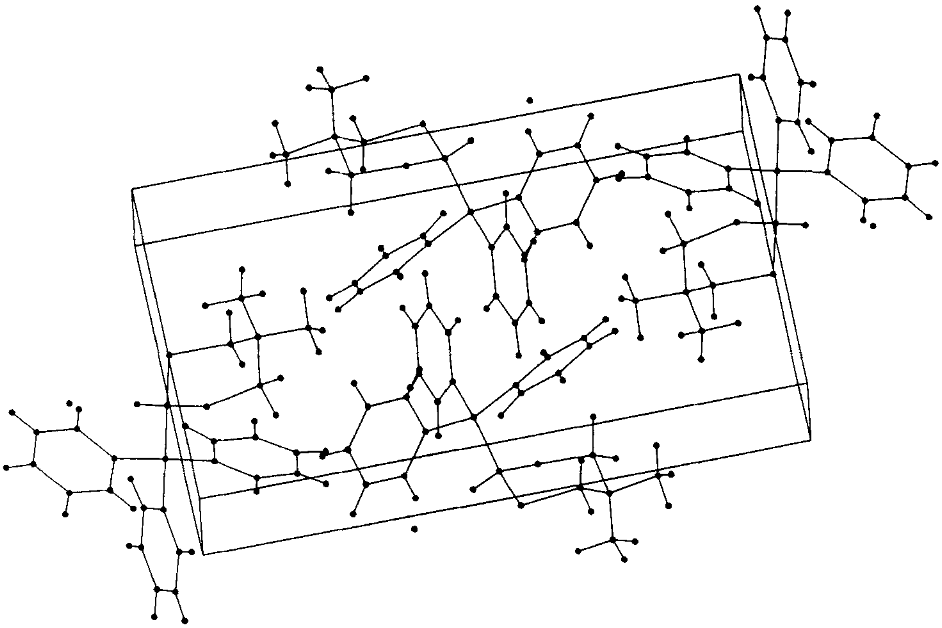


FIGURE 3 The packing of the molecules of **1b** in the unit cell.

atoms were calculated and found to be equal to $\alpha = 39.8°$ and $\beta = 59.2°$, respectively.

It is interesting to note that one of the three P-phenyl rings is situated over the dithiane ring and is almost parallel to the basic plane. The dihedral angle between these two planes is 17.4°. The distances between the discussed phenyl ring and two axial hydrogens at C(2) and C(4) are 2.732 and 2.462 Å, respectively. Most prob-

TABLE I

Crystal data of **1b** and **4b** and experimental details

	1b	**4b**
Molecular formula	$C_{24}H_{26}PS_2Cl$	$C_9H_{20}PS_2Cl$
Crystallization solvent	chloroform/cyclohexane	methanol/ethyl acetate
Space group	$P2_1/c$	$P2_1/n$
a (Å)	13.697(3)	10.437(1)
b (Å)	9.172(3)	11.837(1)
c (Å)	18.822(2)	12.052(1)
β (°)	105.98(1)	112.50(1)
V ($Å^3$)	2273.2(9)	1375.6(3)
Z	4	4
D_c (g/cm^3)	1.30	1.25
μ (cm^{-1})	4.2	61.1
Crystal dimensions (mm)	0.2, 0.3, 0.5	0.3, 0.3, 0.4
Maximum 2θ (°)	60	150
Radiation, λ (Å)	MoKα, 0.71073	CuKα, 1.54178
Scan mode	ω/2θ	ω/2θ
hkl ranges	h= 0 16	h=-13 13
	k= 0 12	k= 0 14
	l=-25 25	l= 0 15
No. of refl. measured	4288	2956
No. of refl.	3992 ($I \geq 1.96\sigma(I)$)	2577 ($I \geq 3\sigma(I)$)
R	0.044	0.046
R_w	0.053	0.047

ably, such a situation is most favorable from the point of view of the repulsive 1,3-*syn*-diaxial interactions.

With regard to the bond lengths in the dithiane ring in **1b**, of interest is that the *endo* S(1)—C(1) and S(2)—C(1) bonds are slightly different (1.817 and 1.808 Å). There is also a substantial difference between the S(1)—C(2) and S(2)—C(4) bond distances of 0.035 Å.

Finally, it should be noted that the chloride anion is situated outside the molecule and its nearest contact of 2.386 Å is with the equatorial hydrogen at C(1).

Crystal and Molecular Structure of **4b**

The X-ray diffraction study of 2-trimethylphosphonio-1,3-dithiane **4b**, the results of which are collected in Table I and Tables VI–IX, showed that the six-membered ring exists in a chair conformation (Figure 4). However, in contrast to **1b**, the trimethylphosphonium group at C(2) in **4b** is occupying the equatorial position. The angle between the C(2)—P bond and the basic S(1), S(2), C(4), C(6) plane

TABLE II

Atomic coordinates of **1b** multiplied by 10^4 (for Cl, P and S by 10^5, for H by 10^3)

Atom	X	Y	Z	Atom	X	Y	Z
Cl	97095(6)	4733(8)	65892(4)	P	26659(6)	22388(9)	46977(4)
S(1)	31420(7)	-8655(9)	51226(4)	S(2)	13777(7)	6447(10)	55573(4)
C(1)	2149(2)	511(3)	4920(1)	C(2)	3661(3)	-750(4)	6118(2)
C(3)	2909(3)	-951(4)	6575(2)	C(4)	2234(3)	440(4)	6454(2)
C(5)	2362(4)	-2341(5)	6466(2)	C(6)	3540(4)	-804(5)	7389(2)
C(7)	3103(2)	1990(3)	3885(1)	C(8)	3716(3)	3057(3)	3701(2)
C(9)	3986(3)	2953(4)	3049(2)	C(10)	3667(3)	1789(4)	2578(2)
C(11)	3057(3)	720(4)	2759(2)	C(12)	2765(3)	810(4)	3407(2)
C(13)	1713(2)	3631(3)	4507(1)	C(14)	693(2)	3268(3)	4216(2)
C(15)	-26(3)	4368(4)	4039(2)	C(16)	259(3)	5821(4)	4135(2)
C(17)	1269(3)	6185(3)	4415(2)	C(18)	1996(3)	5109(3)	4604(2)
C(19)	3706(2)	2795(3)	5458(1)	C(20)	3503(3)	3509(3)	6058(2)
C(21)	4277(3)	3750(4)	6696(2)	C(22)	5256(3)	3287(4)	6736(2)
C(23)	5471(3)	2598(4)	6144(2)	C(24)	4696(3)	2346(4)	5500(2)
H(61)	397(3)	-190(5)	744(2)	H(52)	183(3)	-240(4)	588(2)
H(53)	187(3)	-244(5)	682(2)	H(62)	296(3)	-75(4)	761(2)
H(63)	391(3)	6(5)	746(2)	H(1)	166(2)	19(3)	445(2)
H(21)	414(2)	-164(4)	620(2)	H(22)	404(3)	2(4)	622(2)
H(41)	271(3)	154(4)	659(2)	H(8)	391(2)	381(3)	400(1)
H(9)	440(2)	368(3)	290(2)	H(10)	386(2)	174(4)	215(2)
H(11)	282(2)	-8(3)	245(2)	H(12)	232(2)	13(3)	351(2)
H(14)	47(2)	225(3)	411(2)	H(15)	-71(2)	412(3)	386(2)
H(16)	-25(2)	655(4)	401(2)	H(17)	147(2)	717(3)	446(2)
H(18)	269(2)	531(3)	479(2)	H(20)	279(2)	380(3)	602(1)
H(21)	414(2)	422(3)	711(2)	H(22)	577(2)	351(3)	719(2)
H(23)	616(2)	222(3)	618(2)	H(24)	484(2)	174(3)	510(2)
H(51)	289(2)	-312(3)	657(2)	H(42)	183(2)	27(3)	681(2)

was found to be 88.7°. The Newman projection around the C(2)—P bond (Figure 5) indicates that the exocyclic C(9)—P bond is symmetrically situated between the two endocyclic sulfur atoms S(1) and S(2).

The deformations of the dithiane ring in **4b** in relation to the plane of symmetry are shown below.

$$\Delta C_S^{(C6)} = 2.3(2);\ \Delta C_S^{(C5)} = 0.9(2);\ \Delta C_S^{(C4)} = 3.2(2).$$

The two-fold symmetry parameters are calculated and are as follows:

$$\Delta C_2^{(C4\text{-}S1)} = 2.6(2);\ \Delta C_2^{(C5\text{-}C4)} = 3.0(2);\ \Delta C_2^{(C6\text{-}C5)} = 2.9(2).$$

The values of the α and β angles characterizing the deviations of the six-membered heterocyclic ring in **4b** from an ideal chair conformation are 61.2° and 54.7°, respectively.

The packing of the molecules of **4b** in the crystal is shown in Figure 6. The nearest contact of the chloride anion of 2.604 Å is with the axial hydrogen at C(2).

^{31}P *CP/MAS NMR Studies of* **1b** *and* **4b**

Figures 7a and 7c display the ^{31}P CP/MAS NMR spectra of **1b** and **4b**, respectively. Under slow rotation (ca. 1.1 kHz) the central lines are flanked by spinning side-

TABLE III

Bond lengths (Å) in **1b**

Bond	D(A)	Bond	D(Å)	Bond	D(Å)
P---C(1)	1.830(3)	C(3)---C(5)	1.465(6)	C(14)---C(15)	1.385(5)
P---C(7)	1.804(3)	C(3)---C(6)	1.544(5)	C(15)---C(16)	1.386(5)
P---C(13)	1.790(3)	C(7)---C(8)	1.394(5)	C(16)---C(17)	1.379(5)
P---C(19)	1.793(3)	C(7)---C(12)	1.402(4)	C(17)---C(18)	1.377(5)
S(1)---C(1)	1.817(3)	C(8)---C(9)	1.379(5)	C(19)---C(20)	1.399(4)
S(1)---C(2)	1.815(3)	C(9)---C(10)	1.380(5)	C(19)---C(24)	1.399(5)
S(2)---C(1)	1.808(3)	C(10)---C(11)	1.389(5)	C(20)---C(21)	1.384(5)
S(2)---C(4)	1.780(4)	C(11)---C(12)	1.388(4)	C(21)---C(22)	1.389(5)
C(2)---C(3)	1.524(5)	C(13)---C(14)	1.392(5)	C(22)---C(23)	1.382(5)
C(3)---C(4)	1.555(5)	C(13)---C(18)	1.409(4)	C(23)---C(24)	1.393(5)

TABLE IV

Bond angles (degrees) in **1b**

Angle		Angle		Angle	
C(1)-P-C(7)	108.9(1)	C(4)-C(3)-C(5)	115.6(3)	C(14)-C(13)-C(18)	119.4(3)
C(1)-P-C(13)	110.9(1)	C(4)-C(3)-C(6)	102.8(3)	C(13)-C(14)-C(15)	119.4(3)
C(1)-P-C(19)	109.6(1)	C(5)-C(3)-C(6)	109.9(3)	C(14)-C(15)-C(16)	120.8(3)
C(7)-P-C(13)	108.3(1)	S(2)-C(4)-C(3)	115.8(3)	C(15)-C(16)-C(17)	120.0(3)
C(7)-P-C(19)	105.6(1)	P-C(7)-C(8)	115.6(2)	C(16)-C(17)-C(18)	120.2(3)
C(13)-P-C(19)	109.4(1)	P-C(7)-C(12)	120.9(2)	C(13)-C(18)-C(17)	120.2(3)
C(1)-S(1)-C(2)	103.5(1)	C(8)-C(7)-C(12)	119.8(3)	P-C(19)-C(20)	119.1(2)
C(1)-S(2)-C(4)	105.6(2)	C(7)-C(8)-C(9)	120.0(3)	P-C(19)-C(24)	120.4(2)
P-C(1)-S(1)	109.6(2)	C(8)-C(9)-C(10)	120.6(3)	C(20)-C(19)-C(24)	119.9(3)
P-C(1)-S(2)	115.2(2)	C(9)-C(10)-C(11)	119.7(3)	C(19)-C(20)-C(21)	120.1(3)
S(1)-C(1)-S(2)	116.6(2)	C(10)-C(11)-C12)	120.7(3)	C(20)-C(21)-C(22)	119.7(3)
S(1)-C(2)-C(3)	116.2(2)	C(7)-C(12)-C(11)	119.1(3)	C(21)-C(22)-C(23)	120.9(3)
C(2)-C(3)-C(4)	106.6(3)	P-C(13)-C(14)	120.4(2)	C(22)-C(23)-C(24)	119.9(3)
C(2)-C(3)-C(5)	115.2(3)	P-C(13)-C(18)	120.1(2)	C(19)-C(24)-C(23)	119.6(3)
C(2)-C(3)-C(6)	105.6(3)				

TABLE V

Torsional angles (degrees) in **1b**

Atoms				Angle	Atoms				Angle
C(2)	S(1)	C(1)	S(2)	-40.7(2)	C(1)	S(2)	C(4)	C(3)	-54.1(3)
C(2)	S(1)	C(1)	P	92.5(2)	S(1)	C(2)	C(3)	C(4)	-71.2(2)
C(2)	S(1)	C(1)	H(1)	-154.9(3)	S(1)	C(2)	C(3)	C(5)	58.6(3)
C(1)	S(1)	C(2)	C(3)	56.3(3)	S(1)	C(2)	C(3)	C(6)	180.0(3)
C(4)	S(2)	C(1)	S(1)	40.7(2)	C(2)	C(3)	C(4)	S(2)	69.6(2)
C(4)	S(2)	C(1)	P	-89.9(2)	C(5)	C(3)	C(4)	S(2)	-59.9(2)
C(4)	S(2)	C(1)	H(1)	155.9(3)	C(6)	C(3)	C(4)	S(2)	-179.6(3)

TABLE VI

Atomic coordinates for the structure **4b**

Atom	X	Y	Z	B(Å^2)
Cl	0.4746(1)	0.31131(9)	0.35824(9)	5.82(2)
S(1)	0.07373(9)	0.41589(8)	0.18428(7)	4.27(2)
S(2)	-0.07918(8)	0.51757(9)	0.32733(7)	4.53(2)
P	0.20836(8)	0.58590(7)	0.37528(7)	3.26(2)
C(1)	-0.3536(5)	0.3728(5)	0.0127(4)	7.6(1)
C(2)	0.0468(3)	0.5399(3)	0.2601(3)	3.37(6)
C(3)	-0.1903(5)	0.2762(4)	0.1982(4)	6.9(1)
C(4)	-0.1014(4)	0.4004(4)	0.0739(3)	4.77(9)
C(5)	-0.2153(4)	0.3835(3)	0.1220(3)	4.75(9)
C(6)	-0.2296(4)	0.4872(4)	0.1924(3)	5.13(9)
C(7)	0.1752(4)	0.7100(3)	0.4440(3)	4.73(9)
C(8)	0.3284(3)	0.6163(3)	0.3071(3)	4.46(8)
C(9)	0.2757(3)	0.4762(3)	0.4827(3)	4.16(8)
H(11)	-0.430(4)	0.356(4)	0.040(4)	6(1)*
H(12)	-0.377(5)	0.447(5)	-0.051(5)	9(2)*
H(13)	-0.342(4)	0.314(4)	-0.018(4)	5(1)*
H(21)	0.014(3)	0.604(3)	0.211(3)	2.3(8)*
H(31)	-0.187(4)	0.202(4)	0.146(4)	6(1)*
H(32)	-0.273(4)	0.254(4)	0.212(4)	5(1)*
H(33)	-0.116(4)	0.279(4)	0.251(4)	6(1)*
H(41)	-0.087(4)	0.321(4)	0.030(3)	4(1)*
H(42)	-0.122(3)	0.456(3)	0.029(3)	1.9(7)*
H(61)	-0.259(4)	0.564(4)	0.140(4)	5(1)*
H(62)	-0.310(4)	0.480(3)	0.225(3)	4(1)*
H(71)	0.118(4)	0.706(4)	0.470(3)	4(1)*
H(72)	0.124(4)	0.775(4)	0.366(4)	5(1)*
H(73)	0.264(4)	0.740(3)	0.501(3)	3.5(9)*
H(81)	0.287(4)	0.679(4)	0.255(4)	5(1)*
H(82)	0.412(4)	0.646(4)	0.364(4)	5(1)*
H(83)	0.359(4)	0.543(4)	0.276(3)	4(1)*
H(91)	0.310(4)	0.415(3)	0.448(3)	4(1)*
H(92)	0.355(4)	0.506(4)	0.549(3)	4(1)*
H(93)	0.211(3)	0.445(3)	0.501(3)	2.8(8)*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B_{11}+b^2B_{22}+c^2B_{33}+abcos\gamma B_{12}+accos\beta B_{13}+bccos\alpha B_{23}]$.

TABLE VII

Bond lengths (Å) in **4b**

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
S(1)	C(2)	1.807(3)	C(1)	H(13)	0.82(5)	C(6)	H(62)	1.06(4)
S(1)	C(4)	1.812(3)	C(2)	H(21)	0.95(3)	C(7)	H(71)	0.78(5)
S(2)	C(2)	1.809(4)	C(3)	C(5)	1.530(6)	C(7)	H(72)	1.18(5)
S(2)	C(6)	1.812(3)	C(3)	H(31)	1.08(5)	C(7)	H(73)	0.99(3)
P	C(2)	1.810(3)	C(3)	H(32)	0.97(5)	C(8)	H(81)	0.96(4)
P	C(7)	1.784(5)	C(3)	H(33)	0.79(4)	C(8)	H(82)	0.94(4)
P	C(8)	1.779(4)	C(4)	C(5)	1.522(6)	C(8)	H(83)	1.04(4)
P	C(9)	1.779(3)	C(4)	H(41)	1.12(4)	C(9)	H(91)	0.98(4)
C(1)	C(5)	1.542(5)	C(4)	H(42)	0.83(3)	C(9)	H(92)	0.97(3)
C(1)	H(11)	1.00(5)	C(5)	C(6)	1.532(7)	C(9)	H(93)	0.87(5)
C(1)	H(12)	1.13(6)	C(6)	H(61)	1.09(4)			

TABLE VIII

Bond angles (degrees) in **4b**

Angle		Angle		Angle	
C(2-)S(1)-C(4)	98.3(2)	C(5)-C(3)-H(32)	112(3)	C(5)-C(6)-H(62)	113(2)
C(2)-S(2)-C(6)	99.0(2)	C(5)-C(3)-H(33)	110(4)	H(61)-C(6)-H(62)	101(3)
C(2)-P-C(7)	108.3(2)	H(31)-C(3)-H(32)	96(4)	P-C(7)-H(71)	117(4)
C(2)-P-C(8)	108.7(2)	H(31)-C(3)-H(33)	105(4)	P-C(7)-H(72)	106(2)
C(2)-P-C(9)	109.3(1)	H(32)-C(3)-H(33)	122(4)	P-C(7)-H(73)	109(2)
C(7)-P-C(8)	110.2(2)	S(1)-C(4)-C(5)	116.8(2)	H(71)-C(7)-H(72)	101(4)
C(7)-P-C(9)	110.9(2)	S(1)-C(4)-H(41)	99(2)	H(71)-C(7)-H(73)	114(4)
C(8)-P-C(9)	109.4(2)	S(1)-C(4)-H(42)	109(3)	H(72)-C(7)-H(73)	111(4)
C(5)-C(1)-H(11)	110(2)	C(5)-C(4)-H(41)	110(2)	P-C(8)-H(81)	103(4)
C(5)-C(1)-H(12)	114(2)	C(5)-C(4)-H(42)	108(3)	P-C(8)-H(82)	111(4)
C(5)-C(1)-H(13)	101(3)	H(41)-C(4)-H(42)	114(3)	P-C(8)-H(83)	111(3)
H(11)-C(1)-H(12)	113(5)	C(1)-C(5)-C(3)	109.5(4)	H(81)-C(8)-H(82)	105(4)
H(11)-C(1)-H(13)	105(5)	C(1)-C(5)-C(4)	107.3(3)	H(81)-C(8)-H(83)	122(4)
H(12)-C(1)-H(13)	113(5)	C(1)-C(5)-C(6)	106.4(3)	H(82)-C(8)-H(83)	104(3)
S(1)-C(2)-S(2)	112.8(2)	C(3)-C(5)-C(4)	111.1(4)	P-C(9)-H(91)	110(2)
S(1)-C(2)-P	110.7(2)	C(3)-C(5)-C(6)	111.4(4)	P-C(9)-H(92)	108(2)
S(1)-C(2)-H(21)	115(2)	C(4)-C(5)-C(6)	111.2(3)	P-C(9)-H(93)	111(2)
S(2)-C(2)-P	108.9(2)	S(2)-C(6)-C(5)	114.9(2)	H(91)-C(9)-H(92)	107(3)
S(2)-C(2)-H(21)	104(2)	S(2)-C(6)-H(61)	108(2)	H(91)-C(9)-H(93)	105(4)
P-C(2)-H(21)	104(2)	S(2)-C(6)-H(62)	104(2)	H(92)-C(9)-H(93)	117(3)
C(5)-C(3)-H(31)	111(3)	C(5)-C(6)-H(61)	115(2)		

TABLE IX

Torsional angles (degrees) in **4b**

Atoms	Angle
C(4)-S(1)-C(2)-S(2)	60.8 (2)
C(4)-S(1)-C(2)-P	-176.8 (2)
C(4)-S(1)-C(2)-H(21)	-59.2 (2.5)
C(2)-S(1)-C(4)-C(5)	-59.7 (3)
C(6)-S(2)-C(2)-S(1)	-62.1 (2)
C(6)-S(2)-C(2)-P	174.6 (2)
C(6)-S(2)-C(2)-H(21)	64.1 (2.1)
C(2)-S(2)-C(6)-C(5)	60.7 (3)
C(7)-P-C(2)-S(1)	178.7(2)
C(7)-P-C(2)-S(2)	-56.7 (2)
C(7)-P-C(2)-H(21)	54.2 (2.2)
C(8)-P-C(2)-S(1)	59.0 (2)
C(8)-P-C(2)-S(2)	-176.4 (2)
C(8)-P-C(2)-H(21)	-65.5 (2.2)
C(9)-P-C(2)-S(1)	-60.4 (2)
C(9)-P-C(2)-S(2)	64.2 (2)
C(9)-P-C(2)-H(21)	175.1 (2.2)
S(1)-C(4)-C(5)-C(1)	179.9 (3)
S(1)-C(4)-C(5)-C(3)	-60.5 (4)
S(1)-C(4)-C(5)-C(6)	64.0 (4)
C(1)-C(5)-C(6)-S(2)	179.6(3)
C(3)-C(5)-C(6)-C(2)	60.4(4)
C(4)-C(5)-C(6)-S(2)	-63.9 (4)

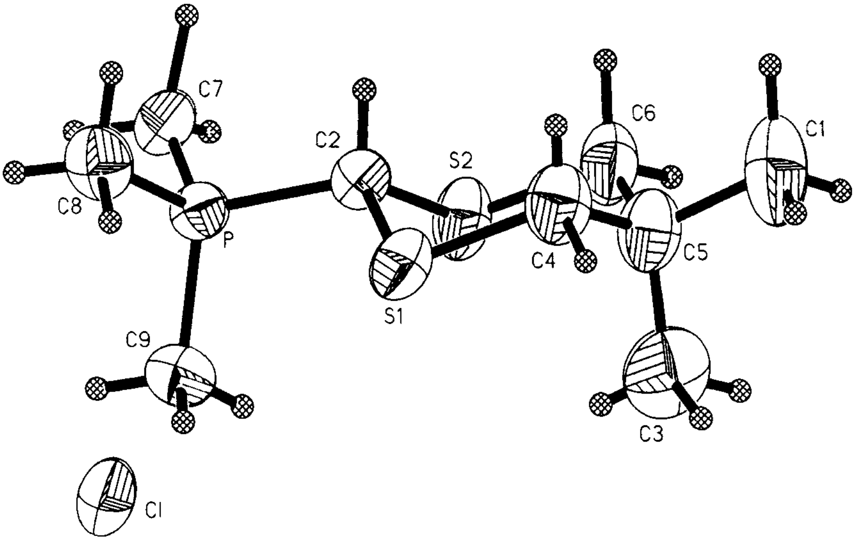


FIGURE 4 The solid state conformation (ORTEP) of the dithiane **4b** with atom numbering system.

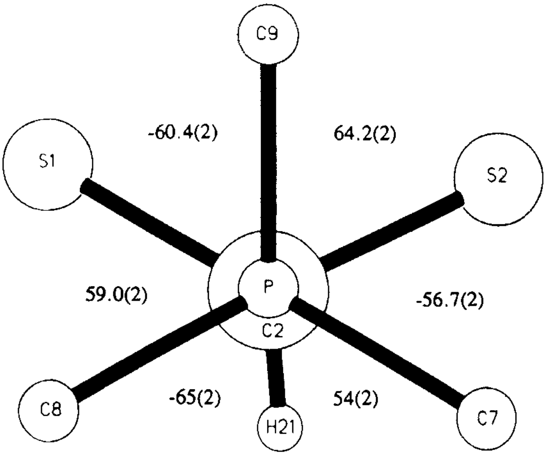


FIGURE 5 The Newman projection around the C(2)—P bond and the relevant torsion angles in **4b**.

bands. The resonances are broadened presumably due to the presence in the crystal lattice of quadrupole (I = 3/2) ^{35}Cl and ^{37}Cl nuclei. As found from X-ray analysis the closest distance between phosphorus and chlorine is larger than 5 Å. Since other adjacent atoms in the tetrahedral arrangement are zero spin nuclei, phosphorus can be considered as an isolated nuclei. The dipolar coupling from phenyl (**1b**) or methyl (**4b**) protons was eliminated by proton decoupling during data acquisition.

With these precautions, employing the MASNMR program based on the Berger and Herzfeld alghoritm from analysis of the spinning sidebands intensities the values of principal components of the ^{31}P chemical shift tensors were obtained.[9,10] The

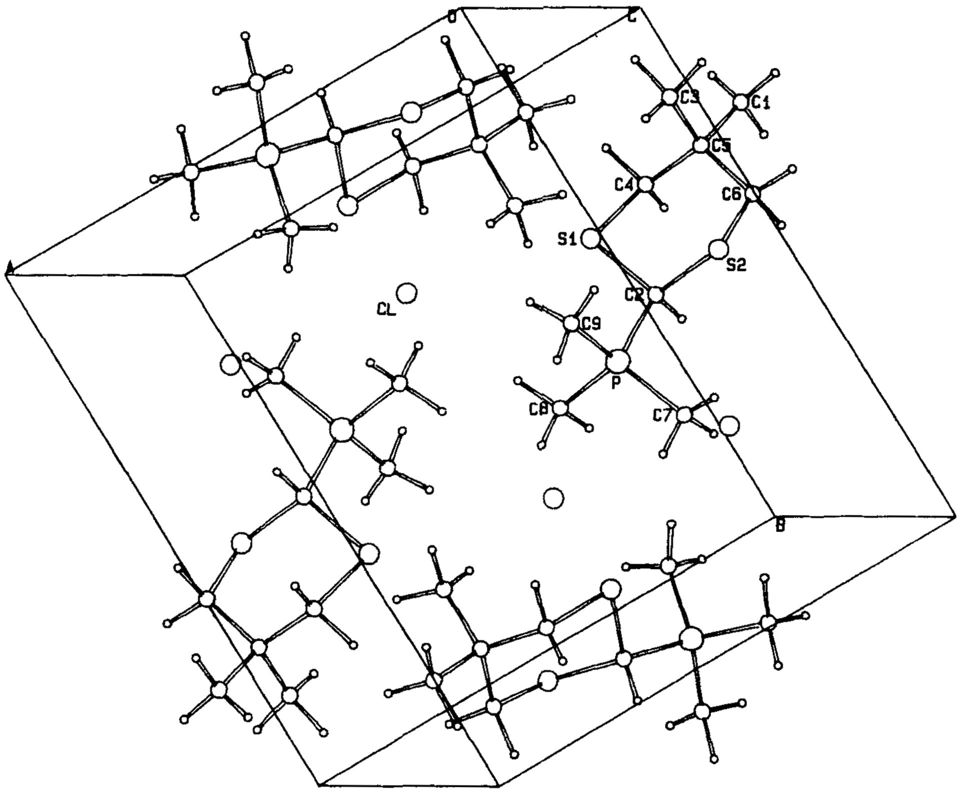


FIGURE 6 The packing of the molecules of **4b** in the unit cell.

calculated principal elements δ_{ii}, anisotropy $\Delta\delta$ and asymmetry η are given in Table X. The accuracy of calculations was confirmed by comparison with theoretical spectra shown in Figure 7b and 7d for compounds **1b** and **4b**, respectively.

DISCUSSION

As was mentioned above, both 2-phosphonio-1,3-dithianes **1b** and **4b** exist in a solution in conformational equilibrium which is shifted towards the equatorial conformation. Therefore, the most important finding of the present study is that the solid state conformation of **1b** is different because the triphenylphosphonium group, Ph_3P^+, is exclusively axial in the crystal. On the contrary, the dithiane **4b** exists in the equatorial conformation.

Although a direct comparison between the Ph_3P^+—C and Me_3P^+—C groupings cannot be made, it is interesting to point out that in the crystal the axial Ph_3P^+—C bond in **1b** of 1.830(3) Å is distinctly longer than the equatorial Me_3P^+—C bond in **4b** [1.810(3) Å]. Moreover, the axial Ph_3P^+—C bond in **1b** is even longer than the axial one in *cis*-5-*t*-butyl-2-triphenylphosphonio-1,3-dithiane **1c** [1.817(4) Å].[5] A comparison of bond distances in the six-membered dithiane rings in **1b** and **4b**

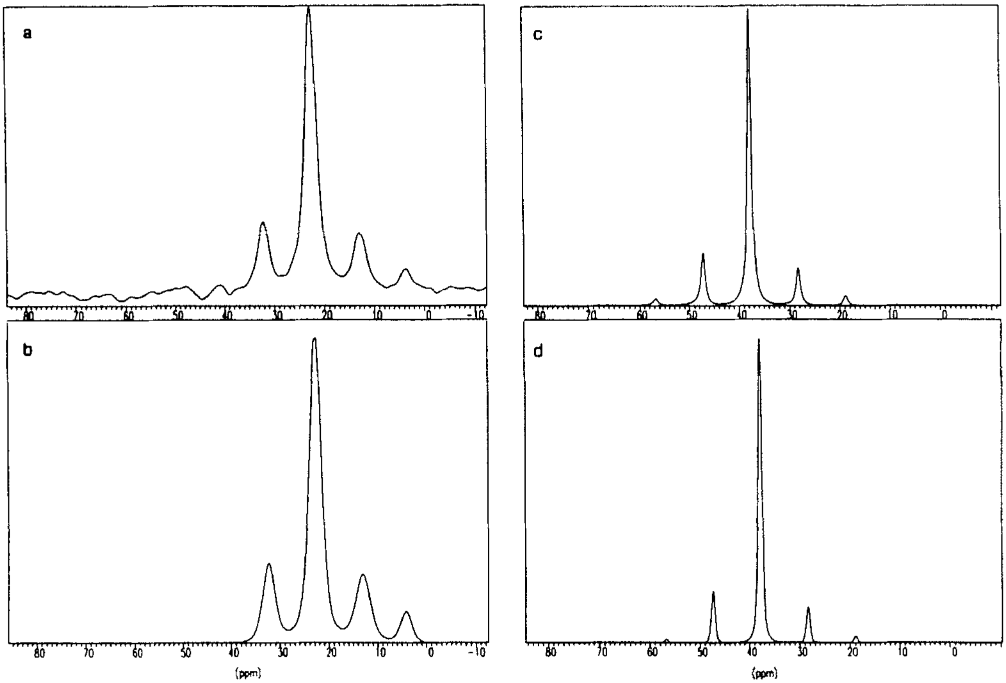


FIGURE 7 Experimental (7a, 7c) and calculated (7b, 7d) ^{31}P CP/MAS NMR spectra of the dithianes **1b** and **4b**.

TABLE X

^{31}P Chemical shift parameters for **1a** and **4b**

Compound	δ_{iso} (ppm) solution	δ_{iso} (ppm) solid	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)	$\Delta\delta$	η
1b	27.35	22.60	37.2	23.3	7.3	-22.9	0.91
4b	37.65	37.80	47.7	40.8	24.7	-19.6	0.53

reveals further interesting differences. Whereas the endocyclic sulfur-carbon bond distances in **1b** are different (vide infra), the corresponding distances in **4b** are almost equal. Assuming that crystal packing forces are not so important as intramolecular interactions, these structural data are consistent with our view and other data[8] that the n_S-σ^*_{C-P} hyperconjugative interaction is one of the factors responsible for the anomeric effect operating in the S—C—P$^+$ system. Thus, in accord with the operation of this stereoelectronic effect one observes in **1b** the shortening of one of the endocyclic anomeric carbon-sulfur bonds and lengthening of the exocyclic axial C—P bond.

Interesting results were also obtained from analysis of ^{31}P chemical shift parameters, in particular, from comparison of isotropic chemical shifts in a solution and the solid state. For **1b** δ_{iso} monitored in chloroform was found to be 27.35 ppm whereas in the solid δ_{iso} is 22.60 ppm. In contrast, for **4b** ^{31}P chemical shifts are very similar in both phases; 37.65 ppm in chloroform and 37.80 ppm in the solid.

Note, that the dithiane **4b** in both phases adopts preferential or exclusive equatorial conformation. However, **1b** is axial in the solid while in a solution conformational equilibrium is shifted towards equatorial conformation. Thus, it is apparent that for **1b** the difference in chemical shifts equal to 4.75 ppm is related to different geometry in both phases.

Further structural information were gained from inspection of anisotropy and asymmetry parameters. Several relationships between ^{31}P shielding parameters and molecular structures of tetracoordinate compounds have been reported. Linear relationship between the asymmetry parameters and intracyclic O—P—O bond angle for series of thiooxyphosphates was found by Dutasta *et al.*[11] Turner and coworkers show that ^{31}P chemical shift anisotropy increases linearly with deviation of the O—P—O angle from the tetrahedral value.[12] Similar conclusion regarding the CSA and degree of departure from cubic symmetry was obtained by Herzfield *et al.*[13] Grimmer observed a linear relationship between the chemical shift anisotropy and P—O bond length for various axially symmetric halogenophosphates.[14] Correlation of ^{31}P chemical shift tensor and shielding parameters with molecular structure of bis(organothiophosphoryl) disulfides was reported by Potrzebowski.[15] The values $\Delta\delta$ found in this work for **1b** and **4b** in the range of 20 ppm, very small compared to other tetracoordinate compounds, suggest that for both compounds local environment of the phosphorus center (C—P—C angles) is close to ideal tetrahedral. These results are in excellent agreement with X-ray data. The differences are seen in asymmetry parameters η, 0.53 for **1b** and 0.91 for **4b**. Unfortunately, having only two measurements we are not in a position to distinguish whether these differences are related to changes of geometry or different character of substituents attached to phosphorus.

EXPERIMENTAL

Crystal Structure Determination of (5,5-Dimethyl-1,3-dithian-2-yl)triphenylphosphonium Chloride **1b**. Single crystals of **1b** were grown from chloroform/cyclohexane solutions. Intensity data were collected on a Syntex $P2_1$ four-circle diffractometer. Measurements were carried out in the $\omega/2\theta$ scan mode for $2\theta_{max} = 60°$ (MoK_α) and no absorption correction was applied. The structure was solved by direct methods using the MULTAN program.[16] Full-matrix refinement of the structure **1b**, with calculation of positional and anisotropic thermal parameters (isotropic thermal parameters for H atoms located from a difference Fourier map) converged to R-factor of 0.043 ($R_w = 0.050$).[18,19]

Crystal Structure Determination of (5,5-Dimethyl-2-dithian-2-yl)trimethylphosphonium Chloride **4b**. The compound was crystallized from methanol with small amounts of ethyl acetate added. Intensity data were collected using a CAD4 diffractometer in the θ range $1 < \theta < 75°$ with graphite monochromatized CuK_α radiation. Lattice constants were refined by least-squares fit of 25 reflections in the θ range 21.8–27.9°. Since a small decline in intensities of three standard reflections ($-3, 4, 4; -1, -1, 6; 4, 1, 2$) was observed (3.9% during 35.9 h), the collected data were corrected by the CHORT program with correction coefficients: min. = 0.9771, max = 1.0441, aver. = 1.0117.[18] Absorption correction was applied by the DIFABS program with correction coefficients: min. = 0.859, max. = 1.454, aver. = 0.989. The structure was solved by direct methods and refined by full matrix least-squares using F's.[17] H atoms were found in a difference Fourier map and refined isotropically. Refinement converged to $R = 0.046$ and $R_w = 0.047$ with unit weight for 198 refined parameters. Largest shift/error in the last cycle was 0.001; largest residual peak in final difference Fourier map was 0.504 eA^{-3}. All calculations were carried out with the Enraf-Nonius SDP crystallographic computing package.[18,19]

NMR Measurements. Cross-polarization magic angle spinning solid state ^{31}P NMR spectra were recorded on Bruker 300 MSL instrument with high-power proton decoupling at 121.496 MHz. Powder samples of **1b** and **4b** were placed in a cylindrical rotor and spun at 1.0–4.5 kHz. For the ^{31}P experiments, the field strength for ^{1}H decoupling was 1.05 mT, a contact time of 5 ms, a repetition of 6 s and spectral width of 50 kHz were used and 8 K data points represented the FID. Spectra were accumulated 100 times which gave reasonable signal-to-noise ratio. ^{31}P chemical shifts were calibrated indirectly through bis(dineo-pentoxythiophosphoryl) disulfide set at 84.0 ppm.

The principal elements of the ^{31}P chemical shift tensor and shielding parameters were calculated employing MASNMR program.

The principal components δ_{ii} were used for calculation of the ^{31}P chemical shift parameters; anisotropy $\Delta\delta$, asymmetry η.

If $|\delta_{11} - \delta_{iso}| > |\delta_{33} - \delta_{iso}|$ then

$$\Delta\delta = \delta_{11} - (\delta_{22} + \delta_{33})/2 \ (1)$$

$$\eta = (\delta_{22} - \delta_{33})/(\delta_{11} - \delta_{iso})(2)$$

If $|\delta_{11} - \delta_{iso}| < |\delta_{33} - \delta_{iso}|$ and $\delta_{11} > \delta_{22} > \delta_{33}$ then

$$\Delta\delta = \delta_{33} - (\delta_{11} + \delta_{22})/2(3)$$

$$\eta = (\delta_{22} - \delta_{11})/(\delta_{33} - \delta_{iso})(4)$$

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