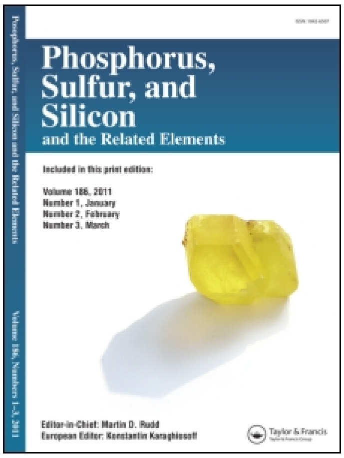

**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# SOLID-STATE NMR STUDIES AND CRYSTAL STRUCTURE OF THE LAWESSON-REAGENT

Gisbert Grossmann[a]; Gisela Ohms[a]; Kerstin Krüger[a]; Gunnar Jeschke[ab]; Peter G. Jones[c]; Axel Fischer[c]
[a] Institut für Analytische Chemie der Technischen Universität Dresden, Dresden, Germany [b] ETH Zürich, Laboratorium für Physikalische Chemie, Zürich [c] Institut für Anorganische und Analytische Chemie der Technischen Universität Braunschweig, Braunschweig, Germany

**To cite this Article** Grossmann, Gisbert , Ohms, Gisela , Krüger, Kerstin , Jeschke, Gunnar , Jones, Peter G. and Fischer, Axel(1995) 'SOLID-STATE NMR STUDIES AND CRYSTAL STRUCTURE OF THE LAWESSON-REAGENT', Phosphorus, Sulfur, and Silicon and the Related Elements, 107: 1, 57 — 68

**To link to this Article: DOI:** 10.1080/10426509508027921

**URL:** http://dx.doi.org/10.1080/10426509508027921

*Phosphorus, Sulfur, and Silicon*, 1995, Vol. 107, pp. 57-68
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# SOLID-STATE NMR STUDIES AND CRYSTAL STRUCTURE OF THE LAWESSON-REAGENT

GISBERT GROSSMANN,* GISELA OHMS, KERSTIN KRÜGER
and GUNNAR JESCHKE†

*Institut für Analytische Chemie der Technischen Universität Dresden,*
*Mommsenstraße 13, D-01062 Dresden, Germany*

and

PETER G. JONES* and AXEL FISCHER

*Institut für Anorganische und Analytische Chemie der Technischen Universität*
*Braunschweig, Postfach 3329, D-38023*
*Braunschweig, Germany*

*(Received June 22, 1995)*

X-ray diffraction of the toluene solvate of the Lawesson reagent, $C_{14}H_{14}O_2P_2S_4.C_7H_8$, gives the following crystal data: triclinic, $P\bar{1}$ (no. 2), a = 6.831 (2), b = 9.393 (3), c = 9.793 (3) Å, $\alpha$ = 70.33 (2), $\beta$ = 83.28 (2), $\gamma$ = 71.35 (2)°, V = 560.6 Å$^3$, Z = 1, and $D_x$ = 1.471 Mg m$^{-3}$. The bond lengths and angles are very close to those observed in the solvent-free crystals. The toluene molecule is disordered over two positions related by an inversion center. The asymmetric unit consists of half the formula unit. This is consistent with the fact that the solid-state $^{31}$P CP MAS NMR spectrum gives one set of principal values of the nuclear magnetic shielding tensor. Similar values were obtained for solvates of other aromatic compounds such as benzene, *o*-dichlorobenzene, methoxybenzene and *p*-dimethoxybenzene. A comparison with the data for the solvent-free Lawesson reagent shows that the nuclear shielding depends not only on the molecular structure but can also be influenced by short intermolecular S···S distances. Results of IGLO calculations of the $^{31}$P nuclear shielding of isolated molecules nevertheless agree satisfactorily with the experimental principal values and also allow the determination of the orientation of the principal axes in the local molecular framework. The IGLO calculations indicate that the axis 3 for the most shielded principal value lies nearly along the P═S bond and that the principal axis 2 is perpendicular to the S═P—C plane.

*Key words:* Lawesson reagent, crystal structure, NMR, chemical shift anisotropy, IGLO calculations.

## INTRODUCTION

2,4-Bis(*p*-methoxyphenyl)-2,4-dithioxo-1,3,2,4-dithiadiphosphetane, well-known as the Lawesson reagent, has found a variety of synthetic applications, e.g. for the thionation of carbonyl functions[1,2] and other reactions.[3] It has proved difficult to obtain good $^{31}$P NMR spectra of this compound because of its poor solubility and high sensitivity to moisture and other solvent impurities. Unambiguous values of the $^{31}$P chemical shift (15 . . . 17 ppm) could only be obtained with the advent of NMR spectrometers using super-conducting magnets.[4] The $^{31}$P NMR lines are strongly

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*Author to whom correspondence should be addressed.

†Present address: ETH Zürich, Laboratorium für Physikalische Chemie, Universitätsstr. 22, CH-8092 Zürich.

shifted to high fields compared to the values of the $RP(S)(SR')_2$ moiety in acyclic compounds[5] of 70–80 ppm. The isotropic $^{31}P$ chemical shift of 44 ppm found for solvent-free Lawesson reagent in the solid state[6] differs to a surprising degree from the value in solution. On the other hand, after recrystallization from benzene[7] or o-dichlorobenzene[8] the isotropic shift decreases to 22.8 and 22.1 ppm, respectively.

It has been reported[9] that some solvents are difficult to remove from the Lawesson reagent after crystallization. The large change in the chemical shift of about 20 ppm in going from the solvent-free to the solvated crystals indicates significant differences in the structure. Since strong deformation of the four-membered ring appears to be unlikely, one is tempted to assume different positions of the phenyl ring with respect to the S═P—C plane.

In spite of the practical interest in this compound, the first crystallographic studies have been reported only very recently for the solvent-free crystals.[10] In this paper we present the crystal structure of the toluene solvate and results of solid-state NMR investigations on crystals of the Lawesson reagent obtained from various aromatic solvents.

In order to determine the orientation of the principal axis system in the molecular framework, which is not available from crystal powder MAS NMR measurements, quantum mechanical calculations of the nuclear magnetic shielding tensors of isolated molecules were performed using the IGLO method.[11]

## RESULTS AND DISCUSSION

### *Crystal Structure of $C_{14}H_{14}O_2P_2S_4 \cdot C_7H_8$*

Atomic coordinates and equivalent isotropic displacement parameters are reported in Table I and the molecular structure (excluding solvent) is shown in Figure 1a. The molecule displays crystallographic inversion symmetry; the phenyl rings are thus necessarily in the trans configuration. The conformation of the molecule is characterized by a dihedral angle of ca. 0° between the phenyl ring and the S═P—C plane (S2—P—C1—C2 − 3.8°) as in the solvent free crystals.[10] Different conformations of the phenyl rings are observed for other aromatic dithiadiphosphetanes. The non-substituted phenyl compound[12] features a dihedral angle of 23° whereas the compounds with 2,4,6-trimethylphenyl[13] groups in trans configuration or 2,4,6-tri-isopropyl-phenyl[14] groups in cis configuration are characterized by angles close to 90°. The orthogonality of the phenyl rings with respect to the S═P—C plane in the latter two cases is a result of the minimization of steric hindrance of the ortho alkyl groups.

The bond lengths and angles in Table II are very close to those observed in the solvent-free crystals.[10] A superposition of both structures is shown in Figure 1b. The only significant difference involves the C—O—C bond angles (117.0 and 119.8°); however, it cannot explain the markedly different $^{31}P$ isotropic chemical shifts of 22.8 and 44 ppm, respectively. The toluene molecule is disordered over two positions related by an inversion center, as indicated in the packing diagram (Figure 2a) by thick and thin lines, respectively.

TABLE I

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$). U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor

| | x | y | z | U(eq) |
|---|---|---|---|---|
| P | 680.0 (12) | 9076.9 (9) | 3999.2 (9) | 24.7 (2) |
| S (1) | -2200.9 (11) | 9901.1 (9) | 4996.3 (9) | 27.8 (2) |
| S (2) | 713.3 (14) | 9782.8 (10) | 1912.6 (9) | 35.4 (2) |
| O | 3656 (4) | 2116 (2) | 6749 (2) | 34.6 (5) |
| C (1) | 1608 (4) | 6977 (3) | 4855 (3) | 22.7 (6) |
| C (2) | 2184 (4) | 5957 (4) | 4016 (3) | 26.1 (6) |
| C (3) | 2855 (5) | 4343 (4) | 4690 (3) | 27.2 (6) |
| C (4) | 2975 (4) | 3722 (3) | 6189 (3) | 24.9 (6) |
| C (5) | 2429 (5) | 4732 (4) | 7027 (3) | 26.1 (6) |
| C (6) | 1747 (5) | 6347 (3) | 6353 (3) | 26.0 (6) |
| C (7) | 3749 (6) | 1450 (4) | 8293 (4) | 38.3 (8) |
| C (91) | 6932 (23) | 6745 (17) | 8605 (14) | 78 (4) |
| C (92) | 5688 (11) | 5706 (8) | 9457 (7) | 38 (2) |
| C (93)' | 6650 (10) | 4090 (8) | 10054 (8) | 43 (3) |
| C (94) | 5514 (19) | 3103 (6) | 10887 (8) | 68 (3) |
| C (95) | 3414 (19) | 3731 (14) | 11124 (8) | 88 (6) |
| C (96) | 2451 (9) | 5347 (15) | 10527 (9) | 72 (4) |
| C (97) | 3588 (11) | 6334 (8) | 9693 (8) | 42 (3) |

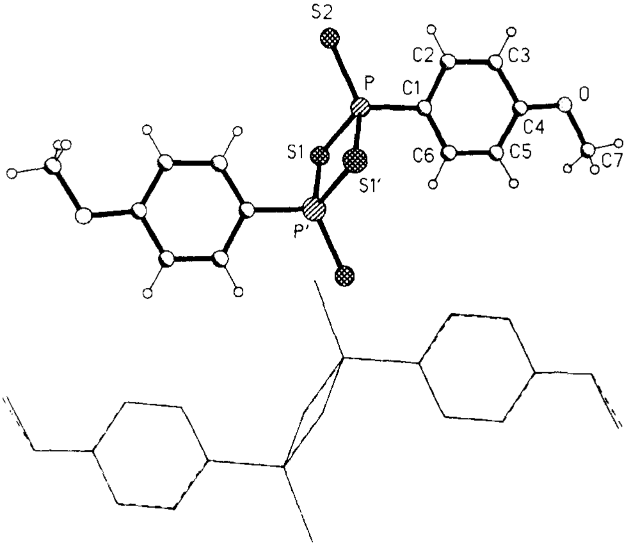

FIGURE 1 The molecular structure (a) of the Lawesson reagent: $C_{14}H_{14}O_2P_2S_4.C_7H_8$ and overlap diagram (b) of structures with toluene (continuous line) and without solvent (broken line).

TABLE II

Selected bond lengths (Å) and angles (°)

| | | | |
|---|---|---|---|
| P–C (1) | 1.791 (3) | P–S (2) | 1.9242 (13) |
| P–S (1) # 1 | 2.1169 (12) | P–S (1) | 2.1238 (12) |
| O–C (4) | 1.359 (3) | O–C (7) | 1.430 (4) |
| C (1) - C (6) | 1.387 (4) | C (1) - C (2) | 1.401 (4) |
| C (2) - C (3) | 1.377 (4) | C (3) - C (4) | 1.386 (4) |
| C (4) - C (5) | 1.392 (4) | C (5) –C (6) | 1.378 (4) |
| C (1) - P - S (2) | 115.66 (11) | C (1) - P - S (1) # 1 | 106.52 (10) |
| S (2) - P - S (1) # 1 | 116.37 (5) | C (1) - P - S (1) | 106.94 (10) |
| S (2) - P - S (1) | 115.82 (6) | S (1) # 1 - P - S (1) | 92.85 (5) |
| P # 1 -S (1) - P | 87.15 | C (4) - O - C (7) | 117.0 (2) |
| C (6) - C (1) - C (2) | 119.5 (3) | C (6) - C (1) - P | 120.3 (2) |
| C (2) - C (1) - P | 120.2 (2) | C (3) - C (2) - C (1) | 119.6 (3) |
| C (2) - C (3) - C (4) | 120.6 (3) | O - C (4) - C (3) | 116.1 (3) |
| O - C (4) - C (5) | 123.9 | C (3) - C (4) - C (5) | 120.0 (3) |
| C (6) - C (5) - C (4) | 119.4 | C (5) - C (6) - C (1) | 120.9 (3) |

Symmetry transformation used to generate equivalent atoms:
# −x,−y+2,−z+1

### *$^{13}$C Solution and Solid-State NMR*

The presence or absence of solvent in the Lawesson reagent after recrystallization is easy to detect by means of solution or solid-state $^{13}$C NMR spectroscopy. From solvents containing a phenyl group, such as benzene, toluene, *o*-dichlorobenzene, methoxybenzene and *p*-dimethoxybenzene, the crystals include solvent in a molar ratio of 1:1, whereas crystallization from $CCl_4$ yields solvent-free Lawesson reagent. In Table III the $^{13}$C NMR data of several solvates and of the solution in $CDCl_3$ are reported.

In solution the carbon atoms C(2), C(6) and C(3), C(5) are chemically equivalent because of sufficiently fast intramolecular rotation around the P—C and the O—$CH_3$ bonds. While five lines would be expected for the X part of an AA′X spin system and six lines if the isotopic effect results in an ABX spin system, only doublets are observed. The reason for this is a broadening of the lines to 7 Hz (full width at half height) for C(3)/C(5), 3 Hz for C(4) and 1.5 Hz for others so that the small P—P coupling constant (<1.5 Hz) cannot be resolved. The fact that the line broadening is strongest for C(3)/C(5) indicates a comparatively slow motion about the C—$OCH_3$ bond. This assumption is corroborated by the differences of the isotropic chemical shifts of C(3) and C(5) in the solid state, where the intramolecular rotations are frozen (see Table III).

All crystals containing the various solvents show very similar isotropic chemical shifts for a given carbon atom. On the other hand notable differences of the chemical shifts $\delta_{iso}$ between these crystals and the solvent-free material are observed for $OCH_3$ and C(2). The differences for $OCH_3$ may well be caused by the different angles C(4)—O—$CH_3$ but the slight change in the molecular structure cannot explain the

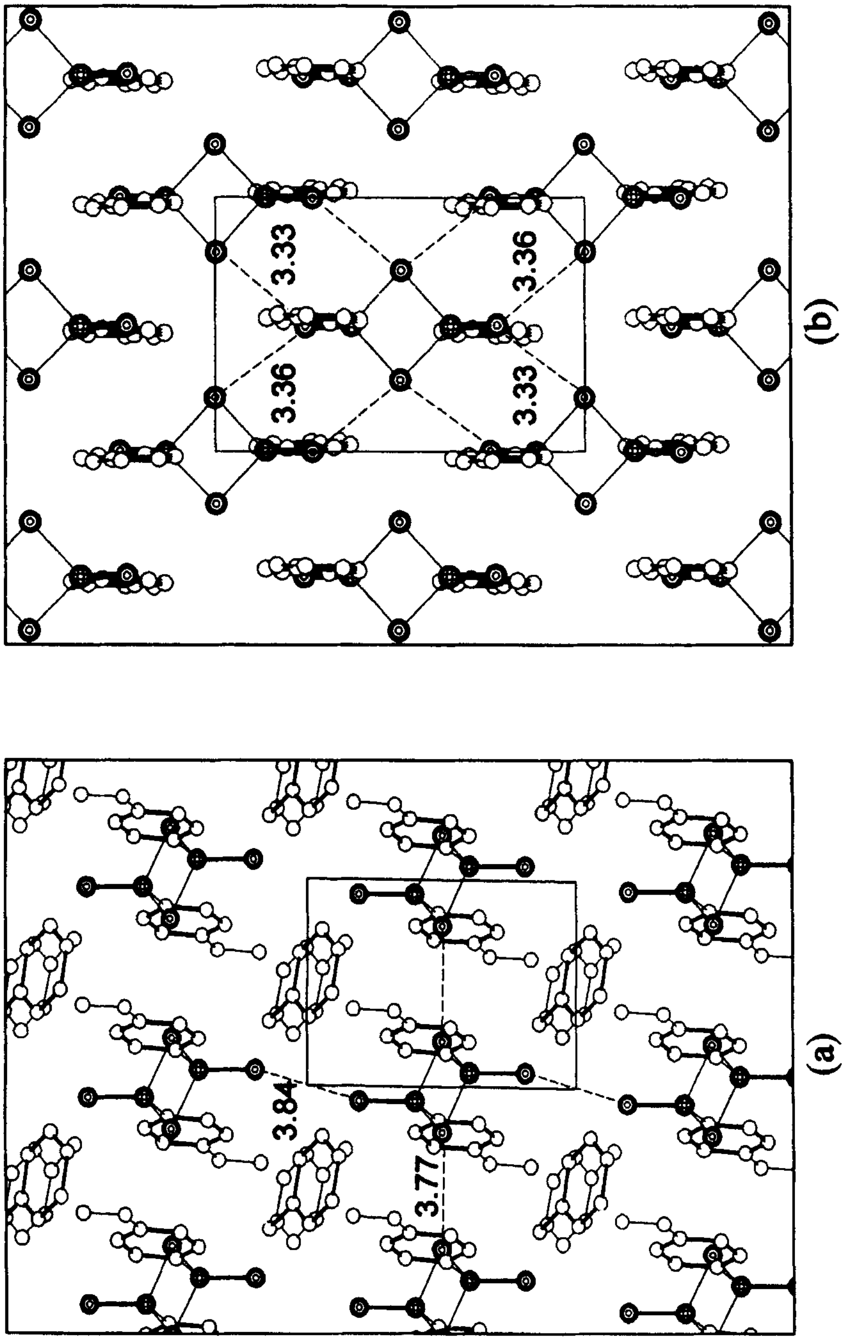

FIGURE 2 The molecular packing (a) of $C_{14}H_{14}O_2P_2S_4.C_7H_8$, view along the crystallographic axis b (the two possible positions of the toluene molecule are indicated by thick and thin lines) and the molecular packing (b) of solvent free Lawesson reagent,[10] $C_{14}H_{14}O_2P_2S_4$, view along the crystallographic axis a.

TABLE III

$^{13}C$ NMR data of Lawesson reagent (LR) in solid state and in solution

| State | $\delta_{iso}$ or $\delta_{sol}$ $^{n}J_{PC}(n)$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | *C1* | *C2* | *C6* | *C3* | *C5* | *C4* | *$CH_3$* | *C(i) in solvent molecules* |
| Solid LR[a] | 130.6<br>90 (1) | 138.8 | 134.2 | 116.8 | 109.9 | 163.8 | 54.8 | - |
| Solid LR.$C_6H_6$ | 128.3<br>95 (1) | 134.7 | 133.3 | 115.2 | 110.5 | 162.9 | 59.9 | 130.3 |
| Solid LR.$C_6H_5CH_3$ | 128.5<br>90 (1) | 134.7 | 133.7 | 115.2 | 110.5 | 162.2 | 59.3 | 139.2 (1), 130.8 (2/3/5/6), 127.0 (4), 25.9 (Me) |
| Solid LR.$C_6H_5OCH_3$ | 128.3<br>95 (1) | 133 | 132 | 115.9 | 112.1 | 162.3 | 57.5 | 160.6(1), 112.1(2), 134(3), 121.5(4), 132.5(5), 119.3(6), 59.6(Me)[b] |
| Solid LR.*p*-$C_6H_4(OCH_3)_2$ | 127.8<br>95 (1) | 134 | 133 | 116.6 | 112.5 | 162.4 | 58.9 | 153.9(1/4), 113.7(2/5), 118.9(3/6), 56.8(Me)[c] |
| Solid LR.*o*-$C_6H_4Cl_2$ | 128.3<br>95 (1) | 133.5 | 131.5 | 116.1 | 111.2 | 162.5 | 58.9 | 133.5(1/2/3/6), 131.6(4/5) |
| Solution in $CDCl_3$ | 130.6<br>94.5 (1) | 134.8<br>17.0 (2) | 134.8<br>17.0 (2) | 114.3<br>18.5 (3) | 114.3<br>18.5 (3) | 163.8<br>2.7 (4) | 55.7 | |

[a] Crystallized from $CCl_4$.

[b] The calculated and referenced to $CH_4$ isotropic chemical shifts of anisole are very similar: 164; 114; 134; 123; 134; 123 and 49 ppm (see Ref. [15]).

[c] The isotropic chemical shifts in crystalline *p*-$C_6H_4(OCH_3)_2$ are very similar: 154; 112; 118 and 55 ppm (see Ref. [15]).

significantly different $\delta_{iso}$ of C(2). The chemical shift of this carbon atom may rather depend on the crystal packing, which is substantially different in the two structures. A detailed examination of the intermolecular distances between the carbon atoms of a given molecule and any atoms of other molecules reveals that the shortest distance is 3.39 Å for C(2) to C(4)* in the crystals of $C_{14}H_{14}O_2P_2S_4 \cdot C_7H_8$ containing stacks of anisyl groups of different molecules. However, in the solvent-free crystals no intermolecular distance between C(2) and other atoms is shorter than 3.8 Å. The similarity of chemical shifts in crystals with different solvent molecules (see Table III) indicates that the structures may be independent of the nature of the solvent.

The number of $^{13}C$ signals from the solvent molecule allows some conclusions about the dynamics of these molecules. Fast motion about the $C_6$ axis may explain why only one signal is observed for the benzene solvate. The two possible positions of the toluene molecule in $LR.C_6H_5CH_3$ are chemically equivalent, as can be seen from the crystal structure. Therefore no information can be obtained from the number of signals on the rate of the motion interchanging these two positions. A similar situation is expected for the other investigated solvents. The fact that seven signals for anisole and four signals for *p*-dimethoxybenzene are observed is evidence for a frozen or sufficiently slow intramolecular motion about the C—$OCH_3$ bonds.

### $^{31}P$ *Solution and Solid-State NMR*

The $^{31}P$ NMR data of solution and solid-state experiments of the Lawesson reagent and the results of IGLO calculations are reported in Table IV. Obviously, the chemical shifts of a compound in various solvents or in the crystalline solid state differ by no more than a few ppm since the nuclear magnetic shielding depends mainly

TABLE IV

$^{31}P$ NMR solution and solid state data of Lawesson reagent (LR) and results of IGLO calculations

| X in solid LR.X | $\delta_{sol}$[a] | $\delta_{iso}$[b] | $\sigma_{11}$ | $\sigma_{22}$ | $\sigma_{33}$ |
|---|---|---|---|---|---|
| $C_6H_6$ | 17.1 | 22.2 | 128 | 187 | 604 |
| $C_6H_5CH_3$ | 17.1 | 22.4 | 131 | 181 | 605 |
| $C_6H_5OCH_3$ | 17.1 | 22.8 | 123 | 186 | 608 |
| *p*-$C_6H_4(OCH_3)_2$ | 17.1 | 22.8 | 133 | 180 | 604 |
| *o*-$C_6H_4Cl_2$[c] | 17.1 | 22.1 | 134 | 185 | 600 |
| -[d] | 17.1 | 43.8 | 134 | 191 | 527 |
| -[e] | - | 41.3 | 143.8 | 191.4 | 524.9 |
| IGLO[f] | - | 21 | 161 | 194 | 566 |
| IGLO[g] | - | 20 | 161 | 196 | 567 |

[a] Solution in $CDCl_3$.
[b] Isotropic chemical shift.
[c] See Ref. [8].
[d] Crystallized from $CCl_4$.
[e] See Ref. [16].
[f] Calculated with the crystallographic coordinates of the solvent free LAWESSON reagent (see Ref. [10]).
[g] Calculated as $LR.C_6H_6$ with the crystallographic coordinates of the toluene solvate of the LAWESSON reagent. The compiled data are mean values of the two phosphorus atoms which are not equivalent since only one benzene molecule was used for the calculation.

on the microstructure around the investigated nucleus and only to a lesser extent on the intermolecular interactions or the rotation and vibration states of the molecule. Therefore, the large difference of ca. 27 ppm in the isotropic part of the chemical shift between the solution and the solvent-free crystals of Lawesson reagent is surprising. After having accidentally obtained a sample containing solvent in the crystals we systematically investigated solvates of the Lawesson reagent obtained by recrystallization from solvents containing a phenyl group. All five solvates have very similar isotropic chemical shifts (ca. 22.5 ppm) that are close to the solution shift of 17 ppm, furthermore no significant differences in the principal values $\sigma_{ii}$ of the nuclear magnetic shielding tensor can be observed. Among the values $\sigma_{ii}$ the most striking is $\sigma_{33}$ with a change of $\Delta\sigma_{33} \approx 70$ ppm in going from solvent-free to solvate crystals (see Figure 3).

The IGLO calculations were performed with the molecular geometries taken from the crystal structures of solvent-free Lawesson reagent and the toluene solvate. In the latter case it was not possible to calculate a cluster with two molecules of toluene forming a symmetrical environment of the investigated molecule, because too many functions are needed. Therefore, a fragment with only one benzene molecule was used. This model leads to two slightly different shielding tensors for the phosphorus atoms. Since the biggest difference of a given $\sigma_{ii}$ value is 7 ppm, mean values are reported in Table IV. A comparison of the last two rows shows that the slight deviations between the two molecular structures cannot explain the large change in the $\sigma_{33}$ value. Therefore it is obvious that the crystal packing influences the chemical shift of the phosphorus atoms. A detailed examination of the intermolecular distances in the solvent-free crystals shows that some S···S distances (3.33 and 3.36 Å) are short compared to the sum of the Van der Waals radii (3.6 Å).[17] In fact the concept of the molecule as a self-contained group of atoms with only very weak interactions to other molecules (neighboring groups of atoms) is no longer a good approximation

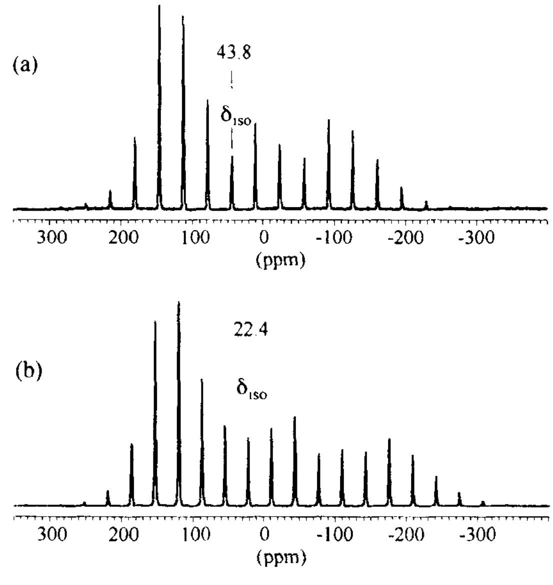

FIGURE 3 $^{31}P$ CP MAS spectra at 121.5 MHz: (a) of $C_{14}H_{14}O_2P_2S_4$ and (b) of $C_{14}H_{14}O_2P_2S_4.C_7H_8$.

here. The short S···S distances should primarily result in a changed distribution of the electron density at the sulfur lone pairs and as a consequence the nuclear magnetic shielding tensor at the investigated phosphorus atom should also change. In contrast, the shortest S···S distances in the toluene solvate are 3.77 and 3.84 Å (Figure 2). In this case the molecule concept is more valid and the nuclear magnetic shielding is expected to be similar to the solution case where the concept also holds. Recently the influence of short intermolecular S···S distances on the $^{31}$P chemical shift tensors was discussed[18] for the compounds *trans*-2,4-diphenyl-1,3,2,4-dithiadiphosphetane and (*cis*)-2,4-dithioxo-2,4-(1,8-naphthalenediyl)-1,3,2,4-dithiadiphosphetane. Quantum chemical model calculations to simulate the intermolecular S···S interaction are now in progress.

Although the deviations of the calculated principal values of the $^{31}$P shielding tensor from the experimental values may be as large as 40 ppm, the calculated tensors reflect the situation satisfactorily. This allows the utilization of another result of these calculations, namely the orientation of the principal axes in the local molecular framework. This orientation cannot be obtained from an analysis of the MAS NMR spectra of crystalline powders, so that the calculations are a substantial complement to the experimental investigations of the nuclear shielding anisotropy. The orientation of the principal axes corresponds to the local structure of the environment of the considered nucleus and hence to its microsymmetry.[19] We define a local molecular framework for any phosphorus atom as follows: the origin is at the $^{31}$P nucleus under consideration, the $z$ axis coincides with the P=S direction, the x axis lies in the S=P—C plane and is directed towards C, whereas the y axis is established by the right-hand rule. The relation between the principal axes 1,2,3 and the local molecular framework x,y,z will be characterized by the angles $\alpha,\beta,\gamma$ (see Figure 4).

The microsymmetry at the phosphorus atoms is close to $C_s$ with the mirror plane coinciding with the S=P—C plane, whereas the small differences between the distances P—S(1) and P—S(1)#1 can be perceived as slight distortions of this mi-

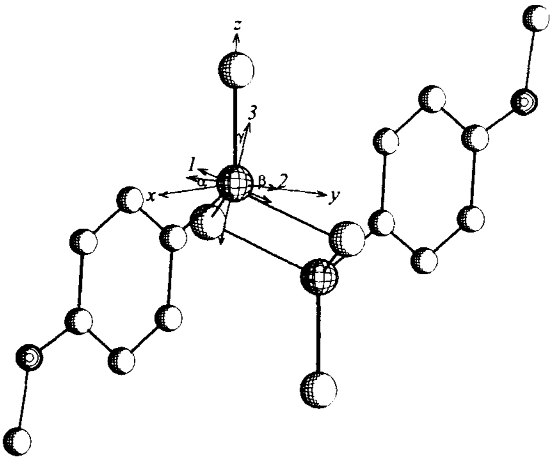

FIGURE 4 By the IGLO method calculated principal axes 1,2,3, the chosen local molecular coordinate system x,y,z and the angles $\alpha,\beta,\gamma$ between these coordinate systems for the Lawesson reagent. $\alpha = 19°$, $\beta = 0°$, $\gamma = 19°$.

crosymmetry. For undistorted $C_s$ microsymmetry one of the principal axes must be perpendicular to the mirror plane. This is the axis 2 as shown in Figure 4. The axes 1 and 3 then lie in the mirror plane, with the latter subtending an angle of 19° with the P═S bond. From experience with other thiophosphoryl compounds[18] we conclude that in four-coordinated phosphorus compounds containing a P═S bond the axis 3 corresponding to the strongest shielding nearly coincides with this bond.

The application of local molecular orbitals (LMOs) within the IGLO scheme[11] allows for an analysis of the individual bond contributions to $\sigma_{ii}$. A detailed discussion of LMO contributions is given in Reference 20 for dithiadiphosphetanes. As can be seen from Table V the contributions of the core electrons are strongly shielding.

The largest deshielding contributions are caused by the P═S, P—S and P—C bonds. If one considers that the deshielding contributions to a given $\sigma_{ii}$ depend on the electronic structure in a plane perpendicular to the principal axis i,[21] bonds almost perpendicular to a certain principal axis should deliver the main deshielding contributions to $\sigma_{ii}$. This is in good agreement with the fact that the deshielding contribution of the P═S bond is reflected by $\sigma_{11}$ and $\sigma_{22}$ and the angles 1—P═S and 2—P═S are close to 90°. The deshielding contributions of both P—S bonds are reflected by $\sigma_{33}$ since the angles 3—P—S and 3—P—S′, respectively, come closest to 90°. Strikingly the deshielding contribution of the P—C bond to the $\sigma_{ii}$ are similar while the angles i—P—C differ significantly. Note however, that a discussion of

TABLE V

LMO contributions to the principal values $\sigma_{ii}$ (in ppm) of the molecule of Lawesson reagent and angle (in °) between axis i and P—X bond

| LMO | Chosen LMO contributions | | | Angle between principal axis and P-X bond | | |
|---|---|---|---|---|---|---|
| | $\sigma_{11}$(P-X) | $\sigma_{22}$(P-X) | $\sigma_{33}$(P-X) | *1*-P-X | *2*-P-X | *3*-P-X |
| Core P[a] | 767 | 768 | 811 | | | |
| P=S | -321 | -265 | -22 | 71.0 | 89.7 | 18.9 |
| P-S | -63 | -58 | -112 | 49.7 | 43.5 | 76.2 |
| P-S | -62 | -57 | -112 | 49.7 | 43.4 | 76.5 |
| P-C | -136 | -154 | -111 | 44.5 | 89.8 | 45.5 |
| 3 lp S=[b] | -8 | -3 | 114 | | | |
| 4 lp S-[c] | -12 | -20 | 13 | | | |
| Σ[d] | 165 | 211 | 581 | | | |
| Total[e] | 161 | 194 | 566 | | | |

[a] Core P are the contributions of the K and L shells of the considered phosphorus.
[b] 3 lp S= denotes the sum of contributions of the three lone-pair LMOs of the terminal sulfur atom.
[c] 4 lp S- denotes the sum of the contributions of the lone-pair LMOs of the two ring sulfur atoms.
[d] Σ is the sum of considered LMO contributions.
[e] Total is the sum of all LMO contributions.

LMO contributions to the $\sigma_{ii}$ solely based on geometrical arguments is limited to rather qualitative predictions, since it fails to acknowledge that deshielding contributions also depend on the effective interaction between occupied and low-lying virtual orbitals of proper symmetry.[20]

The dipole-dipole coupling between the two $^{31}P$ nuclei in the Lawesson reagent constitutes a first order contribution to the spin Hamiltonian that allows for an experimental determination of the dipolar coupling constant and of the orientation of the principal axes in relation to the dipole-dipole vector by solid state NMR measurements without sample rotation. Such investigations were performed by Wasylishen *et al.*[22] and with excellent accuracy by Nakai and McDowell[16] for the solvent-free Lawesson reagent (see Table IV). Considering that the computation of MAS spectra is based on the less precisely measurable spinning sideband intensities, the correspondence with our results is sufficiently good. The differences between the orientation of the P···P vector with respect to the principal axes system obtained by IGLO calculations ($\theta = 0°$, $\phi = 70°$) and given in Reference 16 ($\theta = +4°$ or $-4°$, $\phi = 66.5°$) may be caused by intermolecular interactions, which are not considered in the theoretical calculations.

## EXPERIMENTAL

*Preparation*: The Lawesson reagent was synthesized as described by Cava and Levinson.[2] Recrystallization from tetrachloromethane gave the solvent-free product and from benzene, toluene, *o*-dichlorobenzene, methoxybenzene and *p*-dimethoxybenzene the solvates, respectively.

*Crystal structure analysis. Crystal data*: $C_{14}H_{14}O_2P_2S_4.C_7H_8$, $M_r = 496.57$, triclinic, $P\bar{1}$, $a = 6.831(2)$, $b = 9.393(3)$, $c = 9.793(3)$ Å, $\alpha = 70.33(2)$, $\beta = 83.28(2)$, $\gamma = 71.35(2)°$, $V = 560.6$ Å$^3$, $Z = 1$, $D_x = 1.471$ Mg m$^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 0.58$ mm$^{-1}$, $F(000) = 258$, $T = -130°C$.

*Data collection and reduction*: A colourless plate ca. 0.75 × 0.4 × 0.15 mm was mounted in inert oil and transferred to the cold gas stream of the diffractometer (Stoe STADI-4 with Siemens LT-2 low temperature attachment). A total of 2580 unique intensities were measured to $2\theta$ 55°. Cell constants were refined from $\pm\omega$ angles of 50 reflections in the $2\theta$ range 20–25°.

*Structure solution and refinement*: The structure was solved by direct methods and refined on $F^2$ using the program SHELXL-93.[23] The toluene molecule (disordered over an inversion center) was refined with occupation factors 0.5 and idealized ring geometry. H atoms were included using a riding model. The weighting scheme was $w^{-1} = [\sigma^2(F_0^2) + (0.025P)^2 + 0.61P]$, with $P = (F_0^2 + 2F_c^2)/3$. The final $wR(F^2)$ for all reflections was 0.108, with a conventional $R(F)$ of 0.047, for 153 parameters; $S = 1.03$, max. $\Delta/\sigma = 0.001$, max. $\Delta\rho = 0.35$ eÅ$^{-3}$. Final atomic coordinates are given in Table I, with selected bond lengths and angles in Table II.

Full details of the structure determination have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, from where this material can be obtained on quoting the full literature citation and the reference number CSD 401896.

*NMR spectroscopy*: The NMR spectra were recorded using a Bruker MSL 300 (121.5 MHz for $^{31}P$ and 75.5 MHz for $^{13}C$). The $^{31}P$ chemical shifts are relative to 85% phosphoric acid and $^{13}C$ are relative to $SiMe_4$. For the determination of the anisotropy parameters $^{31}P$ CP MAS spectra were measured at spinning frequencies of 3.5–4.5 kHz using cross polarization with a pulse sequence containing two contact pulses.[8] The spinning sideband systems were computed by means of the program WIN-MAS of Jeschke.[24] The standard deviations of the principal values of the chemical shift tensors caused by phase and basis line correction are 2 ppm while the systematical deviations are estimated to 5 ppm. The principal values of the shielding tensors were calculated from the chemical shift tensors[25] with $\sigma_{ii} = 328$ ppm $- \delta_{ii}$ and have been labeled according to the convention $\sigma_{33} \geq \sigma_{22} \geq \sigma_{11}$.

*IGLO calculation*: The calculations were performed with coordinates from the X-ray diffraction studies. In a first step the electronic ground state was calculated with the TURBOMOLE package.[26] The $^{31}P$

shielding tensors were calculated with the direct IGLO program (DIGLO)[27] using the following Huzinaga basis sets[28] (3s) contracted to [2 1] for H, (7s 3p) contracted to [4 1 1 1, 2 1] for C and O, (11s 7p 2d) contracted to [5 1 1 1 1 1 1, 2 1 1 1 1 1, 1 1] for P and S (as d exponents were used 1.40; 0.35 for P, and 1.60; 0.40 for S).

## ACKNOWLEDGEMENTS

The authors are grateful to the research group of Prof. W. Kutzelnigg, Ruhr-Universität Bochum, for the IGLO program package and Dr. U. Fleischer for helpful discussions. This work was financially supported by Deutsche Forschungsgemeinschaft and by Fonds der Chemischen Industrie.

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