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CONFORMATIONAL PROPERTIES OF ORGANYL(ORGANYLCHALCOGENO)ARSINES, $R_nAs(XR')_{3-n}$ (X = S, Se, Te)

II *. DIPOLE MOMENT AND He(I) PHOTOELECTRON SPECTROSCOPIC STUDIES OF DIMETHYL(PHENYLTHIO)ARSINE AND TRIS(PHENYLTHIO)ARSINE

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Summary

The He(I) photoelectron spectra of dimethyl(phenylthio)arsine and tris(phenylthio)arsine and dipole moment data on these compounds in benzene at 25°C were used to investigate the molecular conformations of the molecules. Dipole moment analyses showed that dimethyl(phenylthio)arsine is present in solution as an almost equimolar mixture of two conformers in which the C—S—As group and the vertical of $S—CH_3—CH_3—As$ pyramid lie in one plane. The repulsion of the lone electron pairs on the arsenic and sulfur atoms is minimized in these conformers. The dipole moment for tris(phenylthio)arsine indicates a pyramidal structure of C_{3v} symmetry for this compound with the phenyl groups pointing in the direction of the arsenic atom at the apex of the pyramid.

The four low-energy bands in the photoelectron spectrum of dimethyl(phenylthio)arsine were assigned to the π_a(phenyl) orbital (9.22 eV), the n_{As} orbital (8.78 eV) and the anti-bonding and non-bonding MO's (8.21 eV, 9.75 eV) which were formed by combining the lone pair orbital of sulfur of predominant p-character with the symmetric ring orbitals π_{sym} and π_0. The difference of ~1.5 eV between the ionization energies of these anti- and non-bonding MO's is evi-

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[*] For Part I see ref. 1.

dence for a non-planar conformation about the C_6H_5—S group. The PE spectrum of tris(phenylthio)arsine is very similar to that of dimethyl(phenylthio)arsine in the low-energy region, and supports the conformation deduced from the dipole moment studies.

Introduction

This study is part of an investigation of organyl(organylchalcogeno)arsines, $R_nAs(XR')_{3-n}$ (X = S, Se, Te; $n = 0, 1, 2$; R = alkyl, R′ = aryl) directed toward achieving a better understanding of their spectrochemical and stereochemical properties and, specifically, of the spatial arrangements about the As—X bonds.

We previously described the synthesis [1] and NMR spectroscopic properties [2] of dimethyl(phenylthio)arsine, $(CH_3)_2As—SC_6H_5$, and tris(phenylthio)arsine, $(C_6H_5S)_3As$. This paper is devoted to an interpretation of the results of dipole moment and He(I) photoelectron (PE) spectral measurements of these two compounds in terms of preferred conformations and electronic structures. No information on the stereochemistry of arsenic-chalcogen compounds in solution or in the gas phase appears to be available in the literature, and only a few solid state structures of compounds containing an As—S bond are known [viz. $(CH_3)_4As_2S_2$ [3], 10-phenoxarsine sulfide [4] and $(C_6H_5)_2As_2S_3$ [5]].

Experimental

Dimethyl(phenylthio)arsine and tris(phenylthio)arsine were prepared and purified by previously described methods [1].

The data required for the calculation of the electric dipole moments by the Guggenheim method [6] were determined in benzene solution at 25 ± 0.01°C as described previously [7]. The dipole moments (experimental accuracy ±0.01 D) are shown in Table 1. The PE spectra were recorded on a Perkin-Elmer PS 18 photoelectron spectrometer. The He(I) resonance line at 584 Å (21.21 eV) served as the ionization source. The spectra were calibrated against Ar and Xe lines. The reproducibility was ±0.05 eV, and the accuracy of the ionization energies (IE) was estimated to be ±0.05 eV.

Results and discussion

Dipole moment analysis

Theoretical dipole moment values ($\mu_{calcd.}$) for dimethyl(phenylthio)arsine

TABLE 1

PARAMETERS FOR THE CALCULATION OF DIPOLE MOMENTS FOR DIMETHYL(PHENYLTHIO)ARSINE AND TRIS(PHENYLTHIO)ARSINE IN BENZENE SOLUTION AT 25°C

Compound	$\Sigma(\epsilon_{12}-\epsilon_{10})/\Sigma w_2$	$\Sigma(n_{12}^2-n_{10}^2)/\Sigma w_2$	μ(D)
$(CH_3)_2AsSC_6H_5$	1.79	0.249	1.74
$(C_6H_5S)_3As$	2.81	0.235	3.30

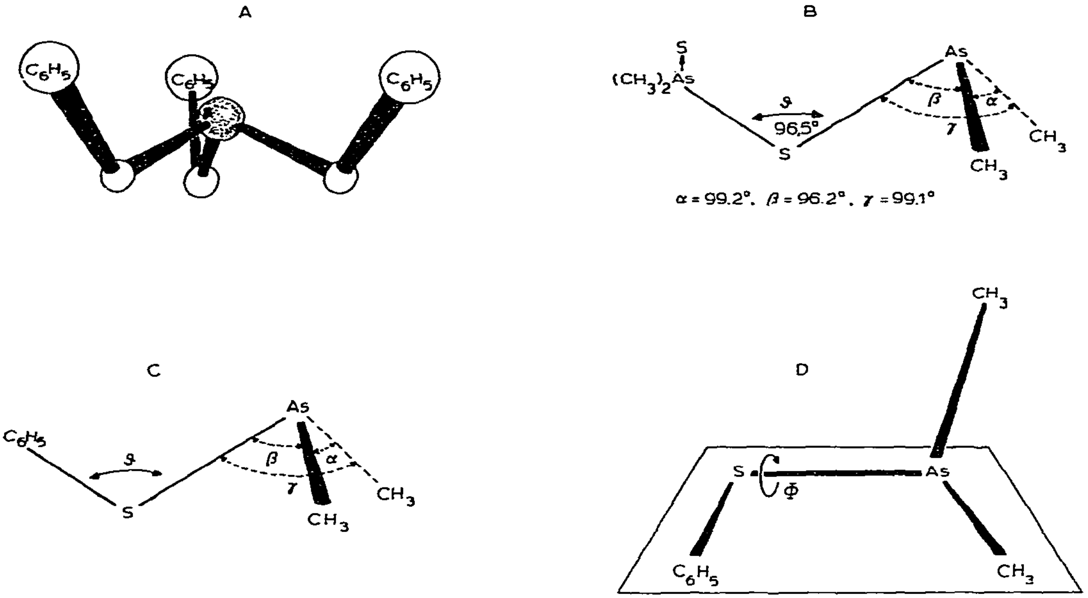

Fig. 1. A, The conformation of tris(phenylthio)arsine. B, The solid-state structure of $(CH_3)_4As_2S_2$. C, Molecular model for dimethyl(phenylthio)arsine in the conformation $\phi = 50.2°$. The C—S—As group is in the plane of the paper, one methyl group is above and the other below this plane, which bisects the CH_3—As—CH_3 angle. D, Molecular model for dimethyl(phenylthio)arsine in the conformation $\Phi = 0°$. The x-y plane, in which the C—S—As—CH_3 group is lying, is the plane of the paper. The z-axis is perpendicular to the plane of the paper with its origin at the arsenic atom.

were obtained by vectorial addition of suitable component bond moments. To derive a reliable As—S bond moment, tris(phenylthio)arsine, the conformation of which (as shown in Fig. 1A) had been unambiguously established on the basis of NMR spectroscopic studies [2], was chosen as the model compound.

Tris(phenylthio)arsine has C_{3v} symmetry. The three planes defined by the As—S—C groups are perpendicular to the base of the trigonal pyramid, which has the arsenic atom at its apex (Fig. 1A). The experimental dipole moment of 3.30 D, which is not affected by torsions of the phenyl groups about the C—S bonds, can be represented as the vectorial sum of the As—S and C—S bond moments (eq. 1). The value μ(C—S) = 1.26 D was derived from the dipole moment

$$\mu((PhS)_3As) = 3[\mu(As{-}S)\cos\omega + \mu(C{-}S)\cos(\vartheta - \omega)] \qquad (1)$$

of diphenyl disulfide [8]. The geometric parameters of tris(phenylthio)arsine were assumed to be those found for $(CH_3)_4As_2S_2$ by X-ray diffraction [3] (Fig. 1B). Thus, the As—S—C angle ϑ was assumed to be 96.5°, equal to the As—S—As angle. The angle ω between the direction of an As—S bond and the threefold symmetry axis of $(C_6H_5S)_3As$ was calculated to be 59.7°. The bond moment μ(As—S) was then obtained as 0.18 D from eq. 1. This value agrees quite well with the previously reported value of 0.15 D deduced from the cyclic compound $As(SCH_2)_3CCH_3$ [9]. The bond moment $\mu(As{-}CH_3)$ = 0.71 D was derived from the dipole moment of trimethylarsine [10].

The dipole moment values for dimethyl(phenylthio)arsine were then obtained by vectorial addition as a function of the angle of rotation Φ about the As—S bond (eq. 2) on the assumption that the geometrical parameters of $(CH_3)_4As_2S_2$ apply also to $(CH_3)_2As—SC_6H_5$ (Fig. 1C) ($\alpha = 99.2°$, $\beta = 96.2°$, $\gamma = 99.1°$, $\vartheta = 96.5°$). The moments μ_x, μ_y, and μ_z in eq. 2 correspond to

$$\mu((CH_3)_2AsSC_6H_5)_{\text{calcd.}} = [\mu_x^2 + \mu_y^2 + \mu_z^2]^{1/2} \qquad (2)$$

the projections of the component moments in the fixed and rotating frames on the chosen coordinate axes (Fig. 1D) and are given by eqs. 3—5. The molecule in the conformation $\Phi = 0$ is shown in Fig. 1D. In this conformation the C—S—As—CH_3

$$\mu_x = \mu(\text{As—S}) + \mu(\text{As—CH}_3)\cos\beta + \mu(\text{As—CH}_3)\cos\gamma + \mu(\text{C—S})\cos\vartheta \qquad (3)$$

$$\mu_y = \mu(\text{As—CH}_3)\sin\beta + \mu(\text{As—CH}_3)[(\cos\alpha - \cos\gamma\cos\beta)/\sin\beta]$$
$$\mu(\text{C—S})\sin\vartheta\cos\Phi \qquad (4)$$

$$\mu_z = (\mu(\text{As—CH}_3)/\sin\beta)(\sin^2\beta\sin^2\gamma - \cos^2\beta\cos^2\gamma - \cos^2\alpha$$
$$+ 2\cos\alpha\cos\beta\cos\gamma)^{1/2} - \mu(\text{C—S})\sin\vartheta\sin\Phi \qquad (5)$$

group lies in the x-y plane with the phenyl group and one methyl group in *cis* position to each other. The x-axis is coincident with the S—As bond. The origin of the coordinate system is at the arsenic atom. The z-axis originating in the arsenic atom is perpendicular to the plane of the paper. The direction of rotation is indicated in Fig. 1D. The angle of rotation Φ is the angle between the C—S—As plane and one of the S—As—CH_3 planes. The difference between β (96.2°) and γ (99.1°), the two S—As—CH_3 angles, is small and hardly influences the results of the computations. The average value of 97.6° was used, therefore, in eqs. 3—5.

The conformation $\Phi = 50.2°$ has the C—S—As group and the vertical of the S—CH_3—CH_3—As pyramid in one plane. In this conformation and the conformation $\Phi = 230.2°$ the orbitals containing the lone electron pairs of the sulfur and the arsenic atoms do not overlap and thus repel each other least. Maximum repulsion is encountered in the conformations $\Phi = 140.2°$ and $\Phi = 320.2°$.

The computations for the rotational angles $\Phi = 230.2°$ and $\Phi = 50.2°$ gave values for $\mu_{\text{calcd.}}$ of 2.15 D and 0.39 D, respectively. The discrepancies between μ_{exp} (1.74 D) and both of the calculated values given above clearly rule out the conformations characterized by $\Phi = 230.2°$ or $\Phi = 50.2°$. Experimental and calculated dipole moments agree for the conformation $\Phi = 156°$, but this conformation seems rather unlikely on energetic grounds.

The repulsions between the lone electron pairs on the arsenic and on the sulfur atoms are minimum in the conformations $\Phi = 230.2$ and $\Phi = 50.2°$, because the angle between the pertinent orbitals is 90°. The interaction between these lobes and the conformational energy is at a maximum when the angle between the orbitals is close or equal to 0°. This conformation is characterized by $\Phi = 140.2°$. The calculated dipole moment for $(CH_3)_2As—SC_6H_5$ on the assumption of free rotation about the As—S bond (1.54 D) is in agreement with μ_{exp} (1.74 D) within the accuracy (±0.2 D) of the additive method of calculating dipole moments. However, free rotation, equivalent to an equal population of all possible conformers, seems unlikely. The energy barrier for a rotation about the As—S bond is probably rather high. It is most likely that a mixture of the two energetically preferred conformations with Φ = 50.2° and 230.2° is present in solution. A mixture of 55% of the conformer Φ = 230.2° and 45% of the conformer Φ = 50.2° has a calculated dipole moment equal to the experimental moment. A definite decision between the "free rotation" model or the "mixture of two conformers" model cannot be made yet. The "mixture of two conformers" model, however, is in the better agreement with energetic considerations outlined above the PE spectroscopic evidence discussed below.

Photoelectron spectra

Figure 2 shows the PE spectra of tris(phenylthio)arsine and dimethyl(phenylthio)arsine in the region of 8 to 13 eV. Below 12.5 eV each spectrum consists of two composite bands located approximately between 8 to 10 and 10.5 12.5 eV.

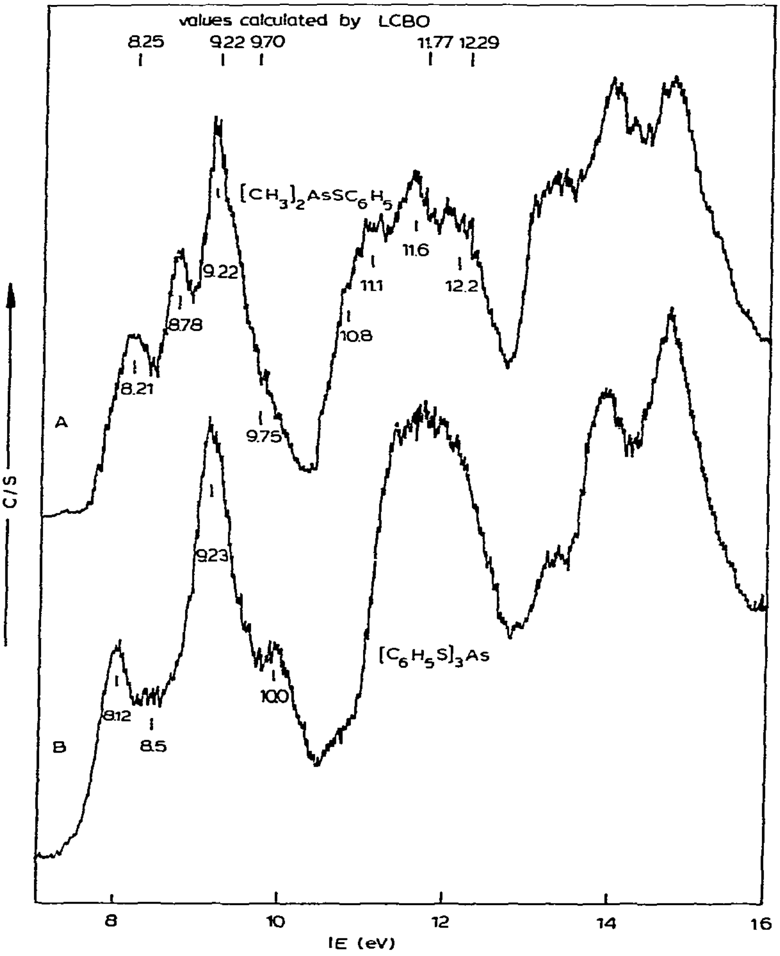

Fig. 2. The photoelectron spectra of tris(phenylthio)arsine and dimethyl(phenylthio)arsine.

The low energy band (8—10 eV) in the spectrum of $(CH_3)_2AsSC_6H_5$ has maxima at 8.21, 8.78 and 9.22 eV and a shoulder at 9.75 eV. Four MO's are expected to contribute to this spectral region in the light of the results of photoelectron investigations of trimethylarsine [11] and thioanisole [12]. The anti-symmetric π-MO (π_a) of the phenyl group causes the maximum at 9.22 eV (IE_3), which is located at 9.28 eV in the spectrum of thioanisole [12]. The $(CH_3)_2AsS$ group thus exerts an inductive effect similar to that of the CH_3S group. The orbital (n_{As}) containing the lone electron pair of the arsenic atom is responsible for IE_2 (8.78 eV), a value very close to the n_{As} ionization energy of 8.65 eV in trimethylarsine [11]. IE_1 (8.21 eV) and IE_4 (9.75 eV) must thus correspond to the anti-bonding and non-bonding MO's of $(CH_3)_2AsSC_6H_5$ which are formed by combining the sulfur lone pair orbital (n_S) of predominant p-character with the two symmetric ring orbitals, π_{sym} and π_0. The difference $IE_4 - IE_1$ of approximately 1.5 eV is considerably smaller than the value of $\approx$2.1 eV found for the planar conformer of thioanisole [12]. It has been shown that this difference decreases when the dihedral angle in thioanisole changes from zero (planar conformation) to 90° (perpendicular conformation) [13]. It is thus likely that in dimethyl(phenylthio)arsine the S—C_6H_5 fragment also adopts a non-planar conformation.

To verify the PE assignments, LCBO calculations were carried out for dimethyl(phenylthio)arsine with special attention to the interactions of the sulfur lone pair orbital (n_S) with the ring orbitals *. The Coulomb integral of π_{sym}, $A_{\pi_{sym}}$, was assumed to be —9.22 eV, equal to the energy of π_a and very close to the corresponding orbital energy in benzene. The integral A_{π_0} was set equal to —12.15 eV, the π_0 energy in benzene. The energies of the two outermost MO's arising from the interaction between n_S and π_{sym} and π_0 orbitals can be taken from the spectrum. From the basis set $A_{\pi_{sym}} = -9.22$ eV, $A_{\pi_0} = -12.15$ eV, $E_1 = -8.21$ eV and $E_2 = -9.75$ eV and the relation for the resonance integrals $B_{n_S/\pi_{sym}} = \sqrt{2}\, B_{n_S/\pi_0}$ the values $A_{n_S} = -8.83$ eV, $B_{n_S/\pi_{sym}} = -0.742$ eV and $E_3 = -12.24$ eV were obtained. The experimental values for planar thioanisole [12] similarly gave $A'_{n_S} = -9.12$ eV, $B_{n_S/\pi_{sym}} = -1.054$ eV and $E_3 = -12.34$ eV. Assuming that the difference between the B values for $(CH_3)_2AsSC_6H_5$ and thioanisole is caused by the non-planarity of the thioarsine, the equation $B_\nu = B_0 \cos \nu$ yielded an angle $\nu = 45°$ between the As—S—C plane and the plane of the phenyl ring. In the conformer with such a large angle ν the interaction between n_S and the ring σ-MO (with an energy of 11.50 eV in benzene) cannot be neglected any more. Thus the value $A_{n_S} = -8.83$ eV calculated as described above does not refer to the sulfur lone pair orbital but rather to its out-of-plane combination with the σ ring orbital. The resonance integral $B_{n_S/\sigma}$ for this interaction can be calculated from data provided by the UPS spectrum of the perpendicular conformer of thioanisole [13]. With $E_1 = -8.55$ eV, $A'_{n_S} = -9.12$ eV (calculated for planar thioanisole) and $A_\sigma = -11.50$ eV the resonance integrals $B_{0(n_S/\sigma)} = -1.297$ eV and $B_{45(n_S/\sigma)} = -0.917$ eV were obtained. The

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* The large size of the molecules investigated prevents the PE assignment being aided by sophisticated calculations. The interaction between the sulfur lone pair (n_S) and the ring orbitals can be investigated with confidence by means of the empirically parametrized LCBO method, which is particularly suitable for accurate reproduction of IE values [14].

Coulomb integral for n_S in $(CH_3)_2AsSC_6H_5$ free from σ mixing ($A^0_{n_S}$) can now be calculated. The determinant gives $A^0_{n_S} = -9.14$ eV. The assumption that

$$\begin{vmatrix} A^0_{n_S} + 8.83 & -0.917 \\ -0.917 & -11.50 + 8.83 \end{vmatrix} = 0 \tag{6}$$

$B_{n_S/\pi_{sym}}$ and $B_{n_S/\sigma}$ in dimethyl(phenylthio)arsine are equal to the corresponding values in thioanisole can now be verified by computing the energies of the MO's formed by the interactions between n_S, π_{sym}, π_0 and σ_{ring} orbitals in $(CH_3)_2AsSC_6H_5$. The basis set $A_{\pi_{sym}} = -9.22$ eV, $A^0_{n_S} = -9.14$ eV, $A_\sigma = -11.50$ eV, $A_{\pi_0} = -12.15$ eV, $B_{n_S/\pi_{sym}} = -0.742$ eV, $B_{n_S/\sigma} = -0.917$ eV and $B_{n_S/\pi_0} = (1/\sqrt{2})B_{n_S/\pi_{sym}} = -0.525$ eV produced the values $E_1 = -8.25$ eV, $E_2 = -9.70$ eV, $E_3 = -11.77$ eV and $E_4 = -12.29$ eV. These calculated energies, shown as bars in Fig. 2, are in good agreement with the experimental data. The assignment of IE_2 (8.78 eV) to the n_{As} ionization is thus confirmed. The similarity of IE_2 to the n_{As} energy in trimethylarsine (8.65 eV) [11] indicates that there is no appreciable interaction between the lone pair orbitals of As and S, as was implicitly assumed in the calculations. These lone pair orbitals must thus be nearly perpendicular to each other.

The two shoulders at 10.8 eV and 11.1 eV on the low energy side of the second band in the spectrum of $(CH_3)_2AsSC_6H_5$ remain to be assigned. On energetic grounds ionization from the σ_{AsC} orbitals is expected to contribute to this region. The bands at 10.7 eV and 11.0 eV in the spectra of phenyl- and benzyldimethylarsine [15] were assigned to σ_{AsC} orbitals, indicating that the two shoulders in the spectrum of the thioarsine also arise from σ_{As} orbitals.

In tris(phenylthio)arsine the three planes formed by the As—S—C groups are perpendicular to the plane containing the three S atoms (Fig. 1A). The sulfur lone pair orbitals lie in the plane formed by the three S atoms. For symmetry reasons, interactions between the sulfur lone pair orbital and the As lone pair orbital are thus not allowed. The distance between the two S atoms is approximately 3.34 Å based on S—As—S angles of ~96° and the As—S single bond lengths of 2.25 Å found in $(CH_3)_4As_2S_2$ [3]. The S—S distances of 3.34 Å, much longer than the S—S bond length of 2.01 Å in diphenyl disulfide [16], largely prevent any interactions between the S atoms.

The low energy region of the PE spectrum of tris(phenylthio)arsine should be very similar to the spectrum of $(CH_3)_2AsSC_6H_5$. The maximum assigned to the n_{As} ionization should be of lower intensity than the bands attributable to n_S and π-ring orbitals. Because σ_{AsC} orbitals are not present in $(C_6H_5S)_3As$ the low energy part of the second band should also have a lower intensity. A comparison of the spectra of $(CH_3)_2AsSC_6H_5$ and $(C_6H_5S)_3As$ (Fig. 2) shows that these expectations are fulfilled, confirming the conformations derived from dipole moments and supporting the assignments in the spectrum of $(CH_3)_2AsSC_6H_5$ of the band at 8.78 eV maximum to n_{As} and the shoulders at 10.8 and 11.1 eV to σ_{AsC}. The difference $IE_4 - IE_1$ (≈1.8 eV) in $(C_6H_5S)_3As$ is 0.3 eV larger than that in $(CH_3)_2AsSC_6H_5$. This indicates that the S—phenyl dihedral angle in $(C_6H_5S)_3As$ is smaller than that in $(CH_3)_2AsSC_6H_5$.

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References

1 R.A. Pyles, K.J. Irgolic and G.C. Pappalardo, J. Organometal. Chem., submitted.
2 K.J. Irgolic, E. Montoneri and G.C. Pappalardo, Spectrochim. Acta, submitted.
3 N. Camerman and J. Trotter, J. Chem. Soc., (1964) 219.
4 W.K. Grindstaff, A.W. Cordes, C.K. Fair, R.W. Perry and L.B. Haudy, Inorg. Chem., 11 (1972) 1852.
5 A.W. Cordes, P.D. Gwinup and M.C. Malmstrom, Inorg. Chem., 11 (1972) 836.
6 E.A. Guggenheim, Trans. Faraday Soc., 45 (1949) 714.
7 G.C. Pappalardo and S. Pistara, J. Chem. Eng. Data, 17 (1972) 2.
8 C.W.N. Cumper, J.F. Read and A.I. Vogel, J. Chem. Soc., (1965) 5860.
9 A.C. Vandenbroucke, Jr., E.J. Boros and J.G. Verkade, Inorg. Chem., 7 (1968) 1469.
10 E.G. Claeys, J. Organometal. Chem., 5 (1966) 446.
11 S. Elbel, H. Bergmann and W. Ensslin, J. Chem. Soc. Faraday II, (1974) 555.
12 H. Bock, G. Wagner and J. Kroner, Chem. Ber., 105 (1972) 3850.
13 A. Schweig and N. Thon, Chem. Phys. Letters 38 (1976) 482.
14 See for example: a) F. Brogli, E. Heilbronner, J. Wirz and E. Kloster-Jensen, Helv. Chim. Acta, 58 (1975) 2620; b) G. Bieri, E. Heilbronner, T.B. Jones, E. Kloster-Jensen and J.P. Maier, Phys. Scripta 16 (1977) 202; c) P. Hemmersback, M. Klessinger and P. Bruckmann, J. Amer. Chem. Soc., 100 (1978) 6344.
15 H. Schmidt, A. Schweig and H. Vermeer, J. Mol. Struct., 37 (1977) 93.
16 B. van Dijk and G.J. Visser, Acta Cryst. B, 27 (1971) 846.