^{117}Sn,^{119}Sn–Proton Long-range Coupling Constants in the ^{1}H Nuclear Magnetic Resonance Spectra of Alkylhalogenostannanes

By G. Barbieri and F. Taddei,* Istituto di Chimica Organica, Università, Via Campi 183, 41100 Modena, Italy

^{1}H N.m.r. spectra of methyl- and ethyl-halogenostannanes have been recorded in [^{2}H]chloroform and [^{2}H$_6$]dimethyl sulphoxide and the parameters obtained by accurate analysis. Large differences in the ^{1}H parameters in the two solvents are found. especially for di- and tri-halogeno-derivatives. Long-range Sn–H coupling constants increase with electronegativity and with the number of halogen atoms. and correlations similar to those obtained for J(^{13}C–H) can be determined for these coupling constants. The spectra for dimethyl sulphoxide solutions and the comparison with those for $CDCl_3$ of methylhalogenostannanes provide information about the *s*-orbital distribution of tin in the Sn–C bonds, it being assumed that the Fermi contact mechanism is the main contribution to long-range tin–proton coupling constants. known geometries of complexes between methyltin halides and sulphoxide being used. In the case of ethyltin derivatives complications arise from the anomalous coupling constants of tin with α-protons which seem very sensitive to the nature of the groups linked to tin.

SEVERAL contributions have been reported relative to the n.m.r. spectra of tetra-alkyltin [1-3] and alkylhalogenostannanes.[4-12] The values of J(Sn–H) have been thought, through the Fermi contact term, to represent [4] a measure of hybridisation at the tin atom. Although this can be roughly true in tetra-alkyltin compounds,[3] the conclusions cannot generally be applied to mixed alkylhalogenostannanes, as is shown by the non-zero intercept found in the approximately linear correlation [13] between J(^{119}Sn–H) and J(^{119}Sn–^{13}C). A similar criticism [7] is based on the observation that a different % *s*-character of tin hybrid orbitals is obtained in R_nSnCl_{4-n} derivatives when R is an ethyl or a methyl group; further, in ethyl derivatives a different % *s*-character is obtained in the same molecule if derived from J(Sn–CH$_3$β) or J(Sn–CH$_2$α); finally, values of more than 100% *s*-character are obtained for $EtSnCl_3$ in water.

Besides the problem of the change in the *s*-character of the tin orbitals bonded to carbon in halogenostannanes, a certain amount of $(d-p)\pi$ interaction could contribute to the bond between tin and halogens; [12] this could, by a synergic process, increase the polarization of the σ-bond between tin and the halogen atom, giving a higher positive charge on the tin atom and thus contracting and stabilizing the *d*-orbitals, which are normally too diffuse for bonding.[14] This fact should be emphasized in polar solvents, since it is known that the tin–halogen bonds have a high dipole moment [15] but the dissociation is very low, as shown by conductivity measurements.[16] On the other hand, in concentrated solution organotin halides undergo an easy halogen–halogen exchange [17] which is probably due to the lower energy of *d*-orbitals and should also be responsible for intermolecular bonding between tin and halogens through $(d-p)\pi$ interactions. The fact that organotin halides behave differently from organotin compounds with four tin–carbon bonds insofar as they give stable co-ordinate (five or six) complexes with ligands such as dimethyl sulphoxide [18] might be explained by this hypothesis. In the latter compounds the synergic mechanism described above should scarcely operate, at least in absence of organic groups containing multiple bonds, where again $(d-p)\pi$ interactions seem to operate.[19-25]

Even if the long-range J(Sn–H) cannot be taken as a quantitative measure of % *s*-character of tin to carbon bond, this value is still to be connected with the hybridization of the tin atom if the Fermi contact term is dominant in describing this coupling mechanism, and this seems to approximate very closely to the case of symmetrical organometal compounds.[26]

We believe, therefore, that long-range coupling constants are a valuable tool in investigating the bond

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between tin and carbon in stannanes and the changes caused by halogen substitution at the tin atom, and particularly in verifying to what extent $(d\text{–}p)\pi$ interactions cause a redistribution of the *s*-orbital of tin in the remaining tin–carbon bonds.

TABLE 1

^{1}H N.m.r. parameters of halogenostannanes Me_nSnHal_{4-n} measured both in $CDCl_3$ and Me_2SO solution

	$CDCl_3$ solution		Me_2SO solution	
Compound.	δ_{CH_3}/ p.p.m.*	$J(^{117}/^{119}Sn\text{–}H)$/ Hz	δ_{CH_3}/ p.p.m.*	$J(^{117}/^{119}Sn\text{–}H)$/ Hz
Me_4Sn	0·07	53·10/55·80	0·05	53·85/56·20
Me_3SnCl	0·69	57·22/59·85	0·55	69·90/72·90
Me_3SnBr	0·79	56·70/59·10	0·69	69·00/72·00
Me_3SnI	0·92	55·95/58·65	0·71	68·40/71·32
Me_3SnPh		54·6 [a]		
Me_2SnCl_2	1·23	66·82/69·82	1·06	112·50/117·75
Me_2SnBr_2	1·44	65·70/68·92	1·29	111·60/117·00
Me_2SnI_2	1·69	61·95/64·50	1·21	109·50/114·15
Me_2SnPh_2	0·46	54·22/57·30	0·52	56·10/58·50
$MeSnCl_3$	1·71	97·72/101·47	0·96	129·75/137·25
$MeSnBr_3$	1·90	86·40/90·18	1·30	124·53/130·35
$MeSnI_3$	2·37	72·90/76·20	1·26	122·37/127·35
$MeSnPh_3$	0·72	54·02/57·00	0·73	55·65/58·50

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* From tetramethylsilane.

For this purpose we have reconsidered the ^{1}H n.m.r. spectra of the methylhalogenostannanes Me_nSnHal_{4-n}, where n = 1, 2, and 3 and the halogen is Cl, Br, and I and the Et_3SnHal, both for [^{2}H]chloroform and [$^2H_6$]dimethyl sulphoxide solution with the intention of discussing the metal–proton coupling constants in the light of the considerations above reported. Measurements were performed for dimethyl sulphoxide since complexation of the halogenostannanes in this solvent is well known [18] and the geometry of the complexes is in some cases established.[27]

RESULTS AND DISCUSSION

^{1}H N.m.r. parameters of the compounds examined are reported in Tables 1—3.[28] We have remeasured these quantities in order to obtain a homogeneous set of results, since accurate values were reported [7-9] for $CDCl_3$ and CCl_4, but not in Me_2SO solution. For the methyl derivatives the parameters were obtained by direct inspection of the spectra which were carefully calibrated, and are the average of several runs. For the ethyl derivatives the parameters were obtained by complete analysis of the A_3B_2 and A_3B_2X systems of main and satellite spectra with the aid of the LAOCN3 computing program.[28] The parameters of these compounds for $CDCl_3$ solution differ slightly from, even if being generally consistent with, those given by Verdonck and Van der Kelen [7,8] and we believe that this could be due to the present more rigorous treatment of experimental data. The parameter error given by the LAOCN3 program never exceeded ±0·1 Hz.

The presence of small quantities of hydrochloric acid could distort the results of the measurements in $CDCl_3$ solution, since it is known that halogenostannanes give rise to halogen–halogen exchange, which is catalysed by the presence of this acid.[19] This effect, however, should be small since our results for methylhalogenostannanes

TABLE 2

Chemical shifts and coupling constants for ethylhalogenostannanes measured in $CDCl_3$ solution

Compound	δ_{CH_2}/p.p.m.*	δ_{CH_3}/p.p.m.*	$J(CH_2\text{–}CH_3)$/Hz	$J(^{117}/^{119}Sn\text{–}CH_2)$/Hz	$J(^{117}/^{119}Sn\text{–}CH_3)$/Hz
Et_4Sn	0·83	1·21	7·9	∓35·1/∓36·5	±65·7/±68·5
$EtSnMe_3$ [a]	0·77	1·14	7·9	∓47·6/∓51·4	±74·5/±77·6
Et_3SnMe [b]	0·83	1·21	8·0	∓37·8/∓38·9	±70·1/±73·0
Et_3SnCl	1·33	1·33	7·7 [c]	∓46·1/∓47·6	±90·8/±94·0
Et_3SnBr	1·34	1·34	7·7 [c]	∓46·4/∓48·1	±90·3/±95·7
Et_3SnI	1·33	1·32	7·9 [c]	∓52·5/∓55·5	±92·9/±96·0
Et_2SnCl_2	1·79	1·43	7·7	∓47·9/∓50·3	±130·3/±135·9

[a] δ_{CH_3} 0·03 p.p.m.; $J(^{117}/^{119}Sn\text{–}CH_{3}\alpha)$ 49·6/51·8 Hz. [b] δ_{CH_3} 0·04 p.p.m. (upfield from tetramethylsilane); $J(^{117}/^{119}Sn\text{–}CH_{3}\alpha)$ 48·1/51·0 Hz. [c] From satellite side bands.

* From tetramethylsilane.

TABLE 3

Chemical shifts and coupling constants for ethylhalogenostannanes measured in dimethyl sulphoxide solution

Compound	δ_{CH_2}/p.p.m.*	δ_{CH_3}/p.p.m.*	$J(CH_2\text{–}CH_3)$/Hz	$J(^{117}/^{119}Sn\text{–}CH_2)$/Hz	$J(^{117}/^{119}Sn\text{–}CH_3)$/Hz
Et_4Sn	0·79	1·20	7·6	∓32·6/∓33·8	±65·3/±67·9
$EtSnMe_3$ [a]	0·83	1·19	8·0	∓48·6/∓51·8	±74·6/±77· 5
Et_3SnMe [b]	0·83	1·21	7·8	∓37·7/∓39·1	±69·6/±72·9
Et_3SnCl	1·07	1·23	8·0	∓68·1/∓71·0	±104·9/±109·2
Et_3SnBr	1·23	1·27	8·0	∓61·0/∓62·5	±99·4/±103·4
Et_3SnI	1·32	1·32	8·0 [c]	∓58·4/∓60·4	±99·3/±103·9
Et_2SnCl_2	1·58	1·28	7·8	∓93·6/∓98·1	±169·8/±177·8

[a] δ_{CH_3} 0·00 p.p.m.; $J(^{117}/^{119}Sn\text{–}CH_{3}\alpha)$ = 50·1/52·4 Hz. [b] δ_{CH_3} = 0·00 p.p.m.; $J(^{117}/^{119}Sn\text{–}CH_{3}\alpha)$ = 48·9/51·5 Hz. [c] From satellite side bands.

* From tetramethylsilane.

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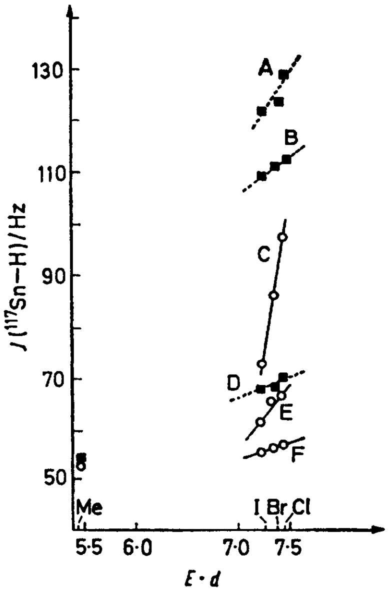
differ only slightly from those of other sources, where the spectra were measured in CCl_4 solution,[4,9,29] and the small differences seem to exclude phenomena associated with the presence of hydrochloric acid in our solutions.

The main feature observed in the trend of long-range coupling constants J(Sn–H) in methylhalogenostannanes is that these quantities increase with electronegativity and the number of halogen atoms attached to tin. In the case of J(^{13}C–H) coupling constants in monosubstituted methanes CH_3X these coupling constants were found to be connected with substituent electronegativity through the product $E_X{\cdot}d_{C-X}$ [30,31] (or more simply $E{\cdot}d$). In our compounds the electronegativity effects can be checked similarly by considering the product $E_X{\cdot}d_{Sn-X}$, where X refers to the group attached to tin in derivatives Me_nSnX_{4-n} ($n = 1, 2,$ and 3) and is equal for Me, Cl, Br, and I. With known bond distances [32] and standard electronegativity values [33] a plot can be constructed as reported in the Figure. It is seen that for the measurements in $CDCl_3$ and Me_2SO solution correlations do not include halogenostannanes and tetramethyltin contemporaneously. Only in the series with the same n do the compounds with different halogen atoms seem to be connected. This indicates that in going from stannanes to halogenostannanes a modification of the electronic structure of the tin atom should occur. This modification has already been invoked and explained in terms of $(d\text{–}p)\pi$ interactions between empty d-orbitals of tin and doubly occupied p-orbitals of halogens.[12] The result of such an interaction should cause a release of the s-orbital from the tin–halogen bond and a redistribution in the remaining tin–carbon bonds, as noted for phosphorus compounds,[34] and, as a consequence of this phenomenon, an increase of the long-range J(Sn–H) should be expected. This kind of perturbation should be different for each halogen. It is expected in fact that a more polar bond should be present when the difference of electronegativity between tin and the halogen is higher; the partial positive charge on the tin atom should make the $(d\text{–}p)\pi$ overlap more efficient.[14] This kind of reasoning leads to the conclusion that the efficiency of this interaction should decrease in the order Cl > Br > I, and, further, should depend strongly on the number of halogen atoms attached to tin, as found experimentally.



Long-range J(^{117}Sn–H) coupling constants in methylhalogenostannanes as a function of the product of Sn–R bond distance (d) and electronegativity of group R (E) where R = Me, Cl, Br, or I. Values labelled ○ were measured for $CDCl_3$ solution and ■ for Me_2SO solution; A, $MeSnHal_3$; B, Me_2SnHal_2; C, $MeSnHal_3$; D, Me_3SnHal; E, Me_2SnHal_2; F, Me_3SnHal

In the spectra of the compounds in dimethyl sulphoxide solution, practically no change is observed for the J(Sn–H) of tetramethyltin while in the halogenostannanes they change markedly especially when two or more halogen atoms are linked to tin. This behaviour is experimentally correlated with the known co-ordination properties of organotin compounds with four carbon–tin bonds and halogenostannanes.[17] Preliminary results [35] on the progressive changes in J(Sn–H), when the formation of complexes between halogenostanannes and dimethyl sulphoxide is followed for the purpose of determining stability constants, have revealed that changes in J(Sn–H) take place even when the co-ordination compound is not yet formed. This has been checked by measuring the i.r. spectra of the solutions of halogenostannanes containing increasing quantities of dimethyl sulphoxide, since the S=O stretching can be observed both for the free and complexed ligand.[27] On the other hand, the results of Peddle and Redl [18] are also a clear indication that complex formation is not a necessary step in the inversion of chiral tin atoms. We believe that the addition of dimethyl sulphoxide should act above all, when present in a small amount, by increasing the polarity of the solution and consequently the degree of $(d\text{–}p)\pi$ interaction in the tin–halogen bond, thus allowing intermolecular bonding even in dilute solutions of non-polar solvents.

The ^{1}H n.m.r. parameters of the compounds in dimethyl sulphoxide solution should represent complete complexation. It is known from X-ray analysis of isolated complexes that a co-ordination with two dimethyl sulphoxide molecules takes place for dihalogenostannanes,[36] with a tetragonal bipyramidal structure, while a trigonal bipyramid is likely to be the structure of

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[31] L. Lunazzi and F. Taddei, *Boll. sci. Fac. Chim. ind. Bologna*, 1965, **23**, 359.

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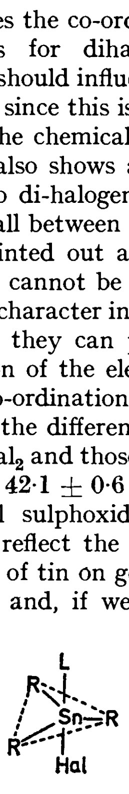
[34] W. McFarlane, J. F. Nixon, and J. R. Swain, *Mol. Phys.*, 1970, **19**, 141.

[35] U. Folli and F. Taddei, results to be published.

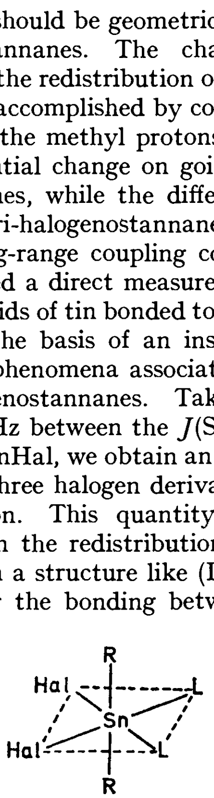
[36] N. Isaacs, C. H. L. Kennard, and W. Kitching, *Chem. Comm.*, 1968, 820.

monoco-ordinate compounds when monohalogenostannanes are involved.[27] The long-range J(Sn–H) measured in dimethyl sulphoxide show a roughly linear dependence, restricted to halogenostannanes, with the product $d{\cdot}E$ (Figure), also restricted to compounds with the same n. These coupling constants change drastically on going from mono- to di-halogenostannanes, while a minor change is observed on going from di- to tri-halogenostannanes. The slopes for these three classes of compound do not differ so strongly as for the measurements in $CDCl_3$ solution. In this solvent the main feature should be represented by the change of co-ordination in mono- and di-halogenostannanes. For trihalogenostannanes the co-ordination should be geometrically the same as for dihalogenostannanes. The change of halogen should influence less the redistribution of the tin s-orbital since this is mainly accomplished by complexation. The chemical shift of the methyl protons in this solvent also shows a substantial change on going from mono- to di-halogenostannanes, while the difference is very small between di- and tri-halogenostannanes.

As pointed out above long-range coupling constants J(Sn–H) cannot be considered a direct measurement of the % s-character in the hybrids of tin bonded to carbon. Even so they can provide the basis of an instructive discussion of the electronic phenomena associated with ligand co-ordination in halogenostannanes. Taking into account the difference in Δ/Hz between the J(Sn–H) of Me_2SnHal_2 and those of Me_3SnHal, we obtain an average value of $42{\cdot}1 \pm 0{\cdot}6$ for the three halogen derivatives in dimethyl sulphoxide solution. This quantity should roughly reflect the change in the redistribution of the s-orbital of tin on going from a structure like (I) to one like (II) and, if we consider the bonding between tin and halogen or a generic ligand to involve only p- or d- (but not s-) orbitals on tin, then the hybrid bonded to carbon should change from sp^2 to sp. Bearing in mind all the changes for the $J(^{117}Sn–H)$ of these complexes thus occasioned we may write, in a very crude approximation of the Fermi contact term,[37] equation (1), where



(I)



(II)

$$\Delta J(^{117}\mathrm{Sn–H}) = \mathrm{const.}\ \Delta\alpha^2 \qquad (1)$$

$\Delta\alpha^2$ is the change in % s-character of the Sn–C bond ($0{\cdot}17$) and the constant is calculated as 248 Hz for Δ/Hz $= 42{\cdot}1$. In order to check this assumption we have determined the $\Delta\alpha^2$ on going from the bypyramid complexes with dimethyl sulphoxide [mean value of $J(^{117}Sn–H)$ for the three halogen derivatives is $69{\cdot}1 \pm 0{\cdot}5$ Hz] and tetramethyltin [$J(^{117}Sn–H) = 53{\cdot}1$ Hz], which can be assumed to have a pure tetrahedral structure. We thus calculate for this compound $\alpha^2 = 0{\cdot}26$ which is very near to the value expected for sp^3 hybridization. For the derivatives $MeSnHal_3$ in Me_2SO solution, values of α^2 are found within the range $0{\cdot}54$—$0{\cdot}51$ which should indicate that substantially the bond between tin and carbon in these derivatives and in this solvent are not too dissimilar from that in the corresponding complexes given by Me_2SnHal_2 derivatives. This result seems more realistic than that found by Holmes and Kaesz[4] and criticized by Verdonck and Van der Kelen.[7] In view of the foregoing, and because of the very approximate nature of equation (1), we do not insist on the numerical aspect of % s-character or on the smaller changes observed within the same series of compounds on changing the halogen, for we do not know the relative importance of the other quantities entering the Fermi contact term, but only the qualitative and useful correlation between % s-character and experimental J(Sn–H) coupling constants.

It thus seems that in the complexed halogenostannanes J(Sn–H) can provide an indication of % s-character in the Sn–C bond, and, very likely for the same compounds in $CDCl_3$ solution, changes of this experimental quantity should be mainly connected with the same kind of perturbation. From the Figure it can be argued that dihalogenostannanes in $CDCl_3$ solution tend to have a distribution of the tin s-orbital in the Sn–C bond similar to 1 : 1 complexes with Me_2SO of monohalogenostannanes. For trihalogenostannanes the situation is slightly different: it is not unlikely that, depending on the nature of the halogen atom, these compounds tend to assume an electronic structure at tin similar to that present in the 1 : 2 complexes of dihalogenostannanes. The changes in monohalogenostannanes should be small and no higher than a few % of s-redistribution in the tin–carbon bonds.

A rapid survey of the results for ethylstannanes reveals that the situation is more intriguing. First the J(Sn–H) for α-CH_2 groups changes appreciably in dimethyl sulphoxide solution on changing the halogen atom and is not virtually constant as it was in α-CH_3 groups. This probably indicates that the changes of this coupling constant on going from the solution in $CDCl_3$ to that in Me_2SO is also sensitive to effects other than complexation; for example, to the nature of the halogen atom. This behaviour is quite different from that observed for the corresponding methyl derivatives. Further, if the long-range coupling constants $J(Sn–CH_2\alpha)$ and $J(Sn–CH_3\beta)$ are employed to derive % s-character of the tin–carbon bonds in the complexes of mono- and di-halogenostannanes with Me_2SO, results similar to those of methylhalogenostannanes are obtained if $J(Sn–CH_3\beta)$ is employed, while a quite different situation (lower % s-character) is obtained when $J(Sn–CH_2\alpha)$ is employed. This, of course, is physically unacceptable, since the two parameters imply two different geometrical arrangements are possible for the same molecule. On

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[37] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon Press, New York, 1966, ch. 3.

the other hand, the behaviour of $J(\text{Sn-CH}_2\alpha)$ in ethyl derivatives is rather different from that of $J(\text{Sn-CH}_3\alpha)$, since the first changes by more than 20 Hz in R_nSnEt_{4-n} on changing the nature of the alkyl group [38] R, while the second varies only by 10 Hz in R_nSnMe_{4-n} derivatives.[38] Further, if a value of $J(\text{Sn-CH}_2\alpha) = 47{\cdot}6$ Hz is chosen, which is that of Me_3SnEt, the % *s*-character in Et_2SnCl_2 obtained from the $J(\text{Sn-CH}_2\alpha)$ in Me_2SO solution is *ca.* 50%, a result which agrees with that obtained from $J(\text{Sn-CH}_3\beta)$ and with that of dimethylhalogenostannanes.

The behaviour of $J(\text{Sn-CH}_3\beta)$ is roughly proportional to that of $J(\text{Sn-CH}_3\alpha)$ in both solvents, while no correlation seems to exist between $J(\text{Sn-CH}_2\alpha)$ and $J(\text{Sn-CH}_3\alpha)$. The discrepancy in the $J(\text{Sn-CH}_2\alpha)$ of ethyltin compounds, which is present also in lead derivatives,[39] is not surprising since these coupling constants seem to be affected strongly by polarity effects, as is shown by correlations with σ^* Taft constants.[38,39] Complexation seems to reduce or mask this effect, making the long-range coupling constants largely dependent on the redistribution of the tin *s*-orbital in the new geometrical situation. Further, conformational effects of the ethyl groups might well be at the root of this anomaly relative to methyl derivatives. Again, the behaviour of $J(\text{Sn-CH}_2\alpha)$ and $J(\text{Sn-CH}_3\beta)$ as a function of $d{\cdot}E$, as discussed for $J(\text{Sn-CH}_3\alpha)$, is not regular, as was that found for Me_nSnX_{4-n} derivatives; in $CDCl_3$ the situation is not clear, while in dimethyl sulphoxide solution both constants increase with the product $d{\cdot}E$ even if not so regularly as in the case of methyl derivatives.

Deeper insight into the situation regarding ethyl derivatives may be acquired by our more extensive study of these compounds in various solvents.

EXPERIMENTAL

The ^1H n.m.r. spectra were recorded at 60 MHz on a JEOL JNM–C60–HL spectrometer in the internal lock mode. The solutions were always freshly prepared with a compound concentration near 0·5M and a small amount of tetramethylsilane was added as a reference peak. Spectra calculation was performed on a CDC 6600 computer. [^2H]Chloroform and [$^2H_6$]dimethyl sulphoxide were commercial solvents from Merck. The compounds were either obtained from Alfa Inorganics or prepared according to known methods.

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