^{1}H and ^{13}C NMR Studies on 1,3,2-Dioxarsolanes

D. W. Aksnes* and A. Lie
Department of Chemistry, University of Bergen, N-5000 Bergen, Norway

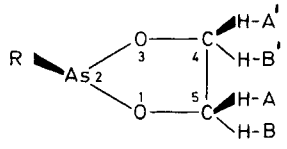
The ^{1}H and ^{13}C NMR spectra of a series of 1,3,2-dioxarsolanes have been obtained at 2.1 T and some at 9.4 T. The chemical shifts and spin–spin coupling constants have been obtained from complete spectral analyses of the ^{1}H and proton-coupled ^{13}C spectra. The spectral data are interpreted on the basis of two rapidly interconverting half-chair conformers with a pseudoaxial substituent at arsenic. Unique assignment of *syn/anti* or *cis/trans* geometries have been made from ^{1}H or ^{13}C NMR spectroscopy alone. The *syn* and *trans* isomers of the 4-methyl- and 4,5-dimethyl-1,3,2-dioxarsolanes, respectively, appear to be conformationally biased towards the forms with pseudoequatorial methyl groups. The general trends in the geminal and vicinal ^{1}H–^{1}H and ^{13}C–^{1}H coupling constants are interpreted in terms of stereospecific, electronegativity and lone-pair effects of the oxygen heteroatoms and conformational factors. The NMR data on the 1,3,2-dioxarsolanes are discussed with reference to related 1,3-dioxa- and 1,3-dithia- five-membered rings with As, P, S or C at the 2-position.

INTRODUCTION

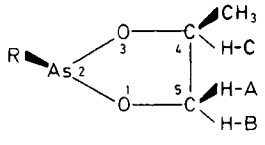
NMR studies of saturated five-membered rings present considerable difficulties owing to the easy interconversions that occur between numerous equienergetic conformers by a pseudorotational mechanism.[1,2] Experimental determinations often do not provide direct evidence for a conclusive description of either a single conformation or of a set of conformations which can better represent the molecule. Although external substituents may prevent complete pseudorotation, conformational changes are still quite easy when one, or even two, small substituents are introduced into the five-membered ring.[3,4]

Previously, studies of molecular conformations of saturated five-membered rings have been largely based on the analysis of vicinal proton–proton coupling constants[2–9] and, in recent years, ^{13}C chemical shifts.[10,11] Unlike ^{13}C shifts, which are easily obtainable from $^{13}C\{^{1}H\}$ spectra, information regarding ^{13}C–^{1}H coupling constants requires the accumulation of proton-coupled spectra, followed by detailed spectral analysis. Usually a prerequisite of such an analysis is a re-analysis of the ^{1}H spectra obtained from the same solution as that for the ^{13}C spectra, since otherwise medium effects may introduce considerable errors.

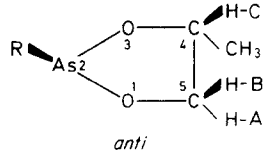
Previous studies of ^{13}C–^{1}H coupling constants on saturated five-membered rings have largely concentrated on one-bond coupling constants, whereas longer range ^{13}C–^{1}H coupling constants have received limited attention, in spite of their potential usefulness.[12] Further, much of the reported data on ^{13}C–^{1}H coupling constants is of doubtful quality, as they have been obtained from a first-order analysis of second-order spectra.



1 R=Cl
2 R=OCH_3
3 R=OPh
4 R=SCH_3
5 R=SPh

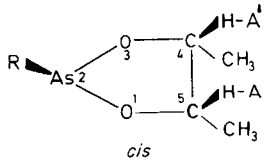


syn

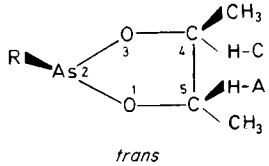


anti

6 R=Cl
7 R=OCH_3
8 R=OPh



cis



trans

9 R=Cl
10 R=OCH_3
11 R=OPh

Scheme 1.

* Author to whom correspondence should be addressed.

CCC-0030–4921/83/0021–0417$04.50

The ^1H NMR spectra of a series of 1,3,2-dioxarsolanes have been reported in preceding papers.[13,14] It has been found that the arsolanes exist in rapidly interconverting nonplanar forms, with a stable configuration at arsenic.

This paper reports the complete spectral analyses of the complex ^1H and proton-coupled ^{13}C spectra of the 1,3,2-dioxarsolanes shown in Scheme 1. The *syn* and *anti* nomenclature refers to the relative orientation of the 2-R and 4-methyl substituents, whereas the *cis* and *trans* configurations define the mutual orientation of the CH_3 groups only.

This series of compounds differs only in the substitution at C-4 and C-5 for a given 2-substituent. It can thus be assumed that conformational changes are mainly localized in the torsional angle of the C-4–C-5 fragment, the geometric properties of the remainder of the molecule being roughly constant.

RESULTS AND DISCUSSION

The ^1H and ^{13}C NMR spectra which were used for the spectral analyses were obtained from the same samples. For the analysis of the ^{13}C spectra it was assumed that the ^1H chemical shifts of the ^{13}C isotopomers are the same as those of the ^{12}C isotopomers. The precision of the resulting parameters, in comparison with the small isotope effect, justifies this assumption.

The ^1H and ^{13}C spectra of **1–5** were analysed as AA'BB' and AA'BB'X spin systems, respectively.

The analyses of the ^1H and ^{13}C spectra of **6–8** were carried out on the basis of $ABCK_3$ and $ABCK_3X$ spin systems, respectively. The analysis of the ^1H and ^{13}C spectra of the 4-methyl compounds obtained at 2.1 T were difficult, owing to partial overlap of spectral lines from the *anti* and *syn* isomers.[13d,e] The ^{13}C spectra of **6–8** were, therefore, re-run at 9.4 T (100.62 MHz) in order to simplify the spectral analysis. At this higher field the ^{13}C spectra of the two isomers were well separated and were nearly first order, with almost identical low- and high-field spectral patterns. It was thus possible to obtain fairly good trial values for the ^{13}C–^1H coupling constants from direct first-order analysis.

The methine and methyl protons and carbons in compounds **9–11** constitute $AA'K_3K_3'$ and $AA'K_3K_3'X$ spin systems for the *cis* isomers, and ABK_3L_3 and ABK_3L_3X spin systems for the *trans* isomers. A slight overlap of lines from the two isomers was observed in the ^1H spectra, whereas the ^{13}C signals of the two isomers were well separated at 2.1 T (Fig. 2).

Careful comparison of trial spectra with the experimental spectra allowed the determination of the starting parameters for all compounds. All ^1H and ^{13}C spectra were subjected to iterative refinements, and the distinct second-order nature of the spectra obtained at 2.1 T yielded the relative signs of the coupling constants. The final parameters, the number of assigned transitions and the RMS errors resulting from the computer analysis are listed in Tables 1–4. Good fits between the observed and simulated spectra were obtained, as shown in Figs 1 and 2.

Precise conformational assignment of the 1,3,2-dioxarsolanes is difficult, and the situation is complicated by the possibility that more than one conformer might be appreciably populated. Therefore, in the discussion which follows, for the sake of simplicity, we shall interpret our results and those of previous work in terms of the rapidly interconverting half-chair forms depicted in Scheme 2. It will be noted that the NMR data are adequately rationalized on the basis of these forms, but the data could also probably fit other conformers.

Table 1. ^1H chemical shifts (ppm from TMS) and ^1H–^1H coupling constants (Hz) in 1,3,2-dioxarsolanes

Parameter	1[a]	2	3	4	5	6[b]	7		8		9[b]		10		11	
							syn	*anti*	*syn*	*anti*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
$\delta_{H\text{-}A}$	4.38	4.08	3.94	4.00	3.99	3.65	3.49	3.36	3.68	3.55	4.53	3.90	4.41	3.82	4.36	3.80
$\delta_{H\text{-}B}$	4.18	3.87	3.75	3.73	3.71	4.34	4.03	4.15	4.22	4.32						
$\delta_{H\text{-}C}$						4.44	4.03	4.37	4.24	4.58		3.90		3.56		3.49
$\delta_{4\text{-}CH_3}$						1.24	1.21	1.10	1.35	1.27	1.08	1.23	1.05	1.23	0.93	1.09
$\delta_{5\text{-}CH_3}$											1.08	1.23	1.05	1.17	0.93	1.04
^2J(H-A, H-B)	−8.90	−8.98	−8.91	−8.90	−8.91	−9.11	−9.15	−8.92	−9.10	−8.73						
^3J(H-A, H-A')	6.31	6.11	6.19	6.02	6.01						5.74		5.33		5.40	
^3J(H-B, H-B')	6.31	6.11	6.14	5.99	5.97											
^3J(H-A, H-B')	6.50	6.36	6.44	6.40	6.40											
^3J(H-A, H-C)						8.93	9.99	7.58	9.87	7.59		9.43		9.01		9.11
^3J(H-B, H-C)						5.74	5.41	5.43	5.56	5.71						
^3J(H-C, CH_3)[c]						6.02	6.02	6.09	6.08	6.03		5.65		6.36		6.07
^3J(H-A, CH_3)[c]											6.41	5.65	6.45	6.07	6.26	6.05
^4J(H-A, CH_3)[c]						−0.04	−0.06	−0.01	−0.06	−0.02	−0.20	0.26	−0.35	−0.13	0.00	−0.17
^4J(H-B, CH_3)[c]						−0.17	−0.13	−0.06	−0.36	−0.06						
^4J(H-C, CH_3)[c]												0.26		0.17		−0.16
No. of assigned transitions		22	22	18	19	73	60	77	85	95	282	340	292	248	186	291
RMS error	0.035	0.013	0.034	0.020	0.019	0.080	0.043	0.035	0.051	0.010	0.077	0.082	0.083	0.097	0.054	0.051

[a] 0.1% in CCl_4.[14] In 70% benzene-d_6 only one peak at δ4.04 is observed.
[b] Averaged spectral parameters due to rapid exchange of chlorine.
[c] CH_3 represents the 4- or 5-methyl group as appropriate.

Table 2. ^{13}C chemical shifts (ppm from TMS) and ^{13}C–^{1}H coupling constants (Hz) of the C-5 carbon in 1,3,2-dioxarsolanes

Parameter	1[a]	2	3	4	5	6[a]	7		8		9[a]		10		11	
							syn	*anti*	*syn*	*anti*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
$\delta_{C\text{-}5}$	68.7	67.8	67.7	67.7	67.5	74.2	73.5	73.8	73.0	73.5	78.8	82.8	77.3	80.6	77.2	80.6
^1J(C-5, H-A)	150.7	147.52	149.09	147.69	147.60	148.33	145.30	146.58	147.16	147.71	149.14	148.20	147.00	145.60	148.43	147.39
^1J(C-5, H-B)	150.7	148.11	149.35	148.59	147.18	149.84	147.64	146.94	148.31	147.93						
^2J(C-5, H-A')	−0.5	−0.35	−0.46	−0.47	−0.28											
^2J(C-5, H-B')	−0.5	−0.89	−0.67	−0.80	−0.78											
^2J(C-5, H-C)						−0.83	−1.61	−0.42	−1.29	−0.25		−3.68		−3.68		−3.63
^2J(C-5, CH_3)[b]												−2.69		−2.83		−2.82
^3J(C-5, CH_3)[c]						5.39	5.69	5.56	5.61	5.49	4.25	5.34	4.25	5.21	4.24	5.32
No. of assigned transitions		18	16	16	16	28	32	40	24	48	137	88	144	64	135	63
RMS error		0.054	0.064	0.074	0.070	0.085	0.036	0.078	0.050	0.062	0.052	0.063	0.054	0.075	0.051	0.065

[a] Averaged spectral parameters due to rapid exchange of chlorine.
[b] Coupling to 5-CH_3.
[c] Coupling to 4-CH_3.

Table 3. ^{13}C chemical shifts (ppm from TMS) and ^{13}C–^{1}H coupling constants (Hz) of the C-4 carbon in 1,3,2-dioxarsolanes

Parameter	6[a,b]	7		8		9[b]		10		11	
		syn	*anti*	*syn*	*anti*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
$\delta_{C\text{-}4}$	77.3	75.8	75.2	76.4	75.2	78.8	82.8	77.3	81.6	77.2	82.1
^1J(C-4, H-C)		147.26	147.74	148.60	148.99		148.20		145.78		147.06
^2J(C-4, H-A)		−2.93	−2.22	−3.25	−1.67	0.22	−3.68	0.19	−3.73	0.20	−3.65
^2J(C-4, H-B)		−0.71	−0.48	−0.69	−0.23						
^2J(C-4, CH_3)[c]		−4.38	−4.41	−4.07	−4.14	−4.26	−2.69	−4.27	−2.21	−4.26	−2.34
^3J(C-4, CH_3)[d]						4.25	5.34	4.25	5.31	4.24	5.24
No. of assigned transitions		32	29	26	24	137	88	144	74	135	64
RMS error		0.039	0.065	0.038	0.061	0.052	0.063	0.054	0.084	0.051	0.074

[a] The spectrum is not analysed owing to poorly resolved lines.
[b] Averaged parameters due to rapid exchange of chlorine.
[c] Coupling to 4-CH_3.
[d] Coupling to 5-CH_3.

Table 4. ^{13}C chemical shifts (ppm from TMS) and ^{13}C–^{1}H coupling constants (Hz) of the 4- and 5-methyl carbons in 1,3,2-dioxarsolanes

Parameter	6[a]	7		8		9[a]		10		11	
		syn	*anti*	*syn*	*anti*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
$\delta_{4\text{-}CH_3}$	18.7	17.9	19.5	18.6	19.0	16.2	18.5	16.7	18.2	16.4	18.2
$\delta_{5\text{-}CH_3}$						16.2	18.5	16.7	18.7	16.4	18.8
^1J($\underline{C}H_3$, CH_3)[b]	127.37	126.84	126.58	127.02	126.81	127.24	127.36	126.51	126.67	126.87	127.01
^1J($\underline{C}H_3$, CH_3)[c]							127.36	126.51	126.63	126.87	127.02
^2J($\underline{C}H_3$, H-A)[c]						−0.12	−0.65	−0.15	−0.23	−0.26	−0.17
^2J($\underline{C}H_3$, H-C)[b]	−0.28	−0.08	−0.01	−0.01	−0.01		−0.65		−0.26		−0.19
^3J($\underline{C}H_3$, H-A)[b]	4.01	3.98	2.58	3.83	2.75	2.14	3.95	2.18	3.68	1.94	3.81
^3J($\underline{C}H_3$, H-B)[b]	1.96	0.74	4.15	0.00	3.89						
^3J($\underline{C}H_3$, H-C)[c]							3.95		3.93		3.67
^4J($\underline{C}H_3$, CH_3)[d]						−0.25		−0.14		−0.14	
No. of assigned transitions[e]	46	48	48	48	48	52	99	96	97 115	98	127 126
RMS error[e]	0.1066	0.066	0.019	0.058	0.031	0.084	0.064	0.109	0.058 0.046	0.094	0.054 0.044

[a] Averaged parameters due to rapid exchange of chlorine.
[b] Coupling from 4-$\underline{C}H_3$.
[c] Coupling from 5-$\underline{C}H_3$.
[d] Coupling between 4-$\underline{C}H_3$ and 5-CH_3. The other four-bond coupling constants are negligible.
[e] Upper line, data for 4-$\underline{C}H_3$; lower line, data for 5-$\underline{C}H_3$.

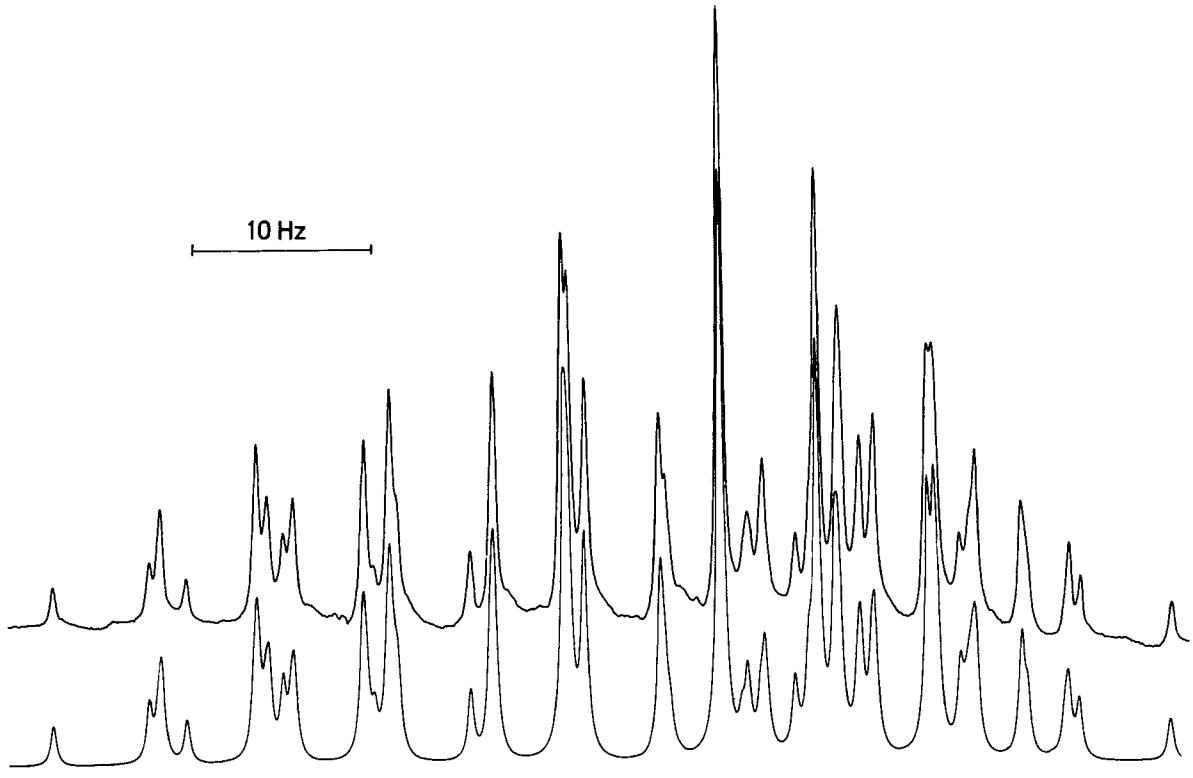
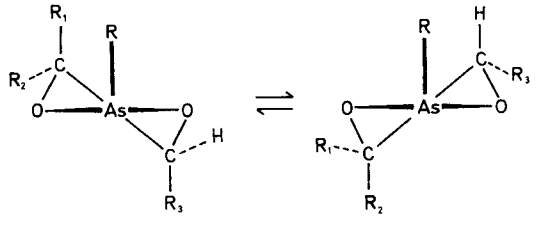


Figure 1. Experimental (upper) and simulated (lower) 90 MHz ^{1}H NMR spectrum of the H-B and H-C region in **7**. The simulated spectrum was calculated for a *syn/anti* distribution of 1 : 1.6.



Scheme 2.

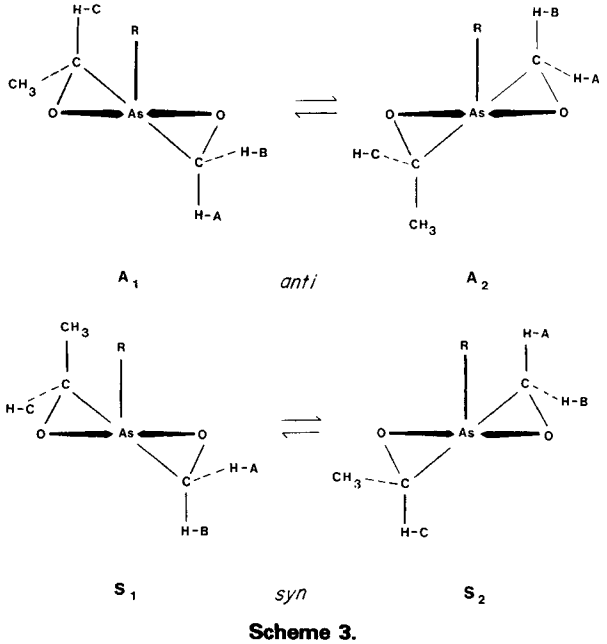
NMR parameters and ring geometry

The methyl proton signals of compounds **6–8** consist of two doublets with intensity ratio *ca* 1 : 1.6.[13e] The low- and high-field resonances have been assigned to the *syn* and *anti* forms, respectively. The predominance of the *anti* isomer in the 4-methylarsolanes[13d,e] and -phospholanes,[6,15,16] in contrast to the situation in 2,4-dialkyl-1,3-dioxolanes,[3,9,10] probably reflects changes in the 1,3-steric interactions as a result of replacing C-2 by a trivalent Group V element.

The *trans* form of compounds **9–11** is unique, whereas the *cis* isomer may exist as *anti* and *syn* forms. However, the ^{1}H and ^{13}C spectra of the *cis* isomer clearly show that only one form, believed to be the *anti* form for steric reasons, is present to a measurable extent. A unique assignment of the *cis* and *trans* ^{1}H and ^{13}C resonance signals is readily made on the basis of the spin systems. The *cis*/*trans* ratio, which varies with the relative amount of *meso*- and *d,l*-butane-2,3-diol used in the preparation, is readily obtained from integration of the methyl or methine proton signals.

^{1}H chemical shifts

The ring proton region at lowest field in **1–5** has been assigned to the protons situated *syn* to the pseudoaxial substituent at arsenic. Downfield shifts of protons *syn* (or *cis*) rather than *anti* (or *trans*) to a pseudoaxial substituent at phosphorus and sulphur have also been postulated for the analogous phospholanes[17] and ethylene sulphite.[17,18] Further support for the '*syn* rule' follows from the very reasonable assignment of



Scheme 3.

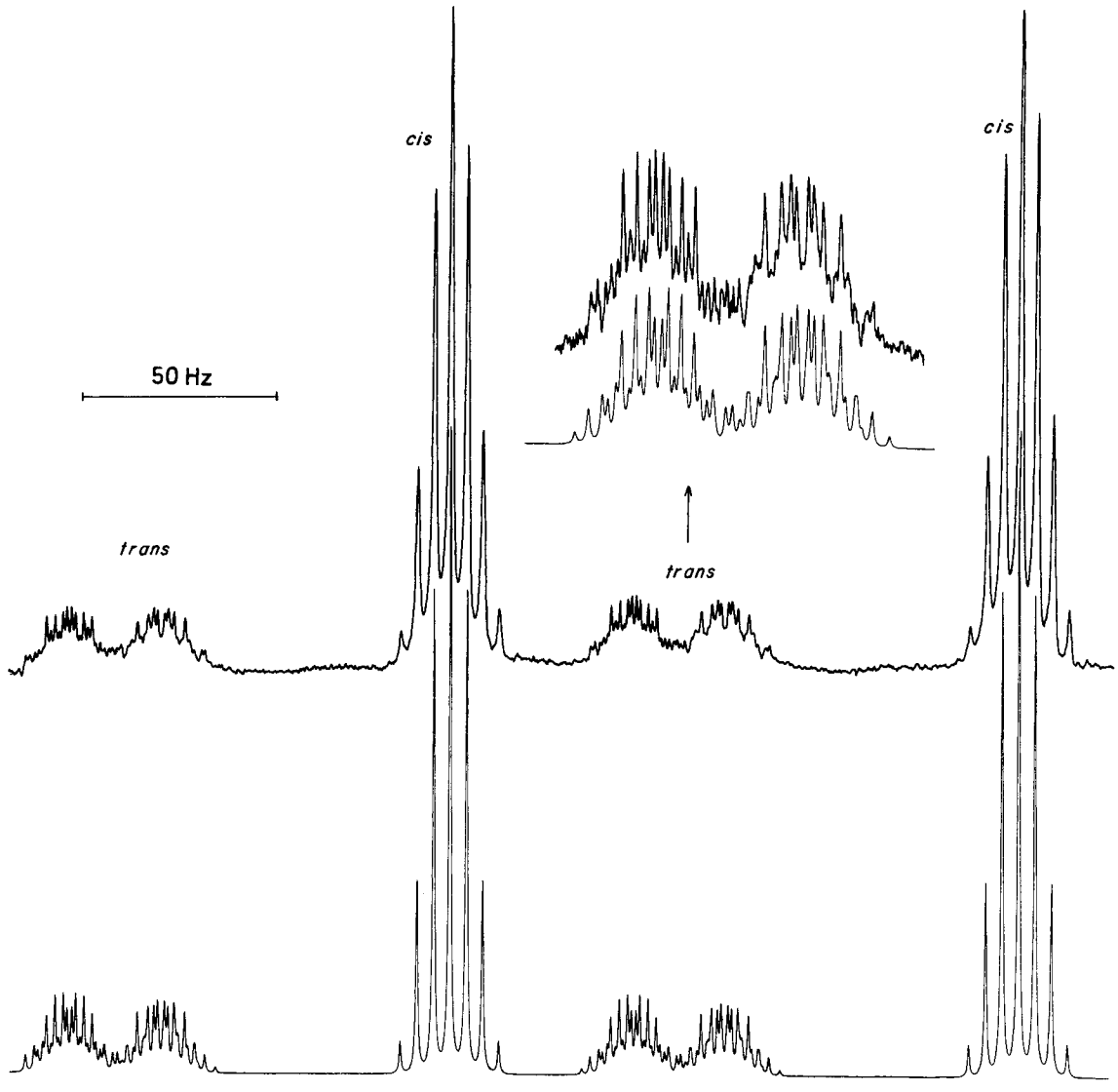


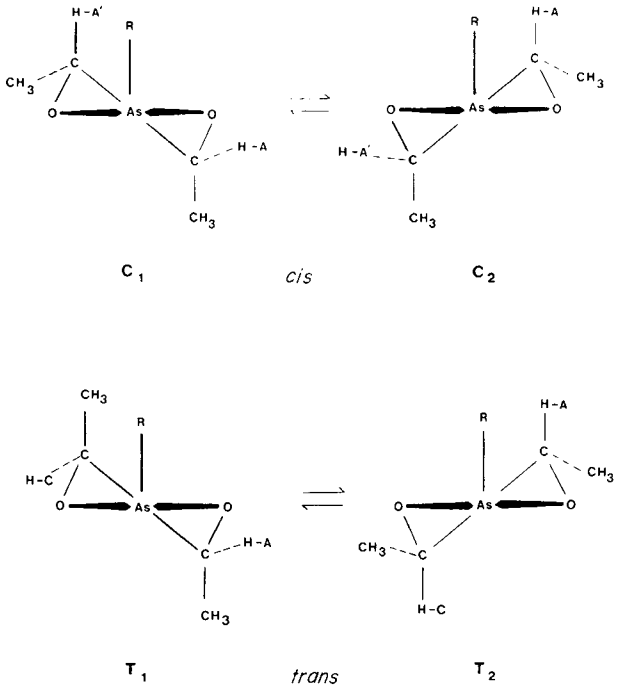
Figure 2. Experimental (upper) and simulated (lower) 22.63 MHz proton-coupled ^{13}C NMR spectrum of the methine carbons in **10**. The simulated spectrum was calculated for a *trans/cis* distribution of 1:2.6.

the proton signals in the geometrical isomers of the methyl-substituted arsolanes.[13d,e] It is thus seen that methyl, methylene and methine protons which have the same relative orientation with respect to the As—R group (*syn* or *anti*) are shifted in the same relative direction, in the absence of other dominant effects (Scheme 1). For example, in the 2-R-4-methyl-1,3,2-dioxarsolanes shown in Scheme 3, (R = Cl, OCH_3, OPh and Ph),[13b] and in the related 1,3,2-dithiarsolanes,[13d] the methyl signals of the *syn* isomers (CH_3 *syn* to As—R) appear at lower field than the methyl signals of the *anti* isomers (CH_3 *anti* to As—R).

However, the relative shifts of the methylene protons in the *syn* isomers (Scheme 3, S_1 and S_2) are not in accordance with the *syn* rule in that the H-A signal appears upfield from the H-B signal. This chemical shift reversal is doubtless caused by the 4-methyl group. In this context, it should be remembered that an equatorial methyl group has been found to produce a considerable upfield shift of the vicinal axial proton in methyl-substituted 1,3,2-dioxarsenanes[19] and 1,3-dioxanes.[20] By analogy, the pseudoaxial H-A proton in the predominating S_2 conformer (see below) should experience an appreciable upfield shift produced by the pseudoequatorial methyl group. On the basis of the observed moderate shift effects of axial methyl groups on vicinal methylene protons in 1,3-dioxanes,[20] the pseudoaxial methyl group in S_1 is expected to shift the H-A and H-B resonances only slightly in the upfield and downfield directions, respectively. The net result for the 4-methyl substituent is a reversal of the chemical shifts of the methylene protons in the *syn* molecules compared with the unsubstituted arsolanes.

In the *anti* conformers (Scheme 3, A_1 and A_2) the paramagnetic effect of the As—R group and the vicinal methyl interaction probably pull in the same direction. In accordance with this assumption, the H-B signal appears downfield from the H-A signal in all *trans* compounds.

Further evidence for the *syn* rule is found in 2-R-*trans*-4,5-dimethyl-1,3,2-dioxarsolanes (Scheme 4, R = OCH_3, OPh and Ph),[13b] in that the proton resonances of the methyl and methine protons situated *syn*



Scheme 4.

to the As—R group appear downfield from their *anti*-oriented counterparts. In these systems both methine protons are expected to experience similar substituent effects from the vicinal methyl groups.

^{13}C chemical shifts

By comparing compounds differing only in the substituent at arsenic, it is seen that chlorine produces larger downfield shifts on the ring carbons (*ca* 1–2 ppm) than the other substituents, which have very similar effects. In the analogous 1,3,2-dioxaphospholanes,[6,11] the relative effect of the 2-substituent on the ring carbon shieldings is also small.

Syn–anti geometries can also be readily assigned to the 2-R-4-methyl-1,3,2-dioxarsolanes on the basis of the ^{13}C chemical shifts. For the 4-methyl series, the C-4 shift of the *syn* isomer is downfield by 0.6–1.2 ppm of that for the *anti* form, in agreement with that found for the related dithiarsolanes[21] and dioxaphospholanes.[6] This downfield shift is presumably a result of the *syn* 1,3-interaction of the 2-R and 4-methyl substituents.

In the *trans* isomers of **10** and **11**, it is also seen that the C-4 resonance is shifted 1.0–1.5 ppm downfield relative to the C-5 signal. This observation is also consistent with the downfield α-effect produced by a *syn*-substituted methyl group.

The chemical shift effect of methyl substitution on the ring carbons can be evaluated by comparing the ^{13}C chemical shifts of the methyl derivatives with those of the corresponding parent compounds. On the introduction of a 4-methyl group into the five-membered ring, C-4 and C-5 experience α- and β-deshielding effects of 7.4–8.6 and 5.3–6.0 ppm, respectively. Similar α- and β-deshielding effects of a 4-methyl group have been reported for 1,3-dioxolanes (7.6 and 6.3 ppm, respectively).[10]

The downfield shifts of the ring carbons in **9–11** (9.5–14.4 ppm) are similar to those reported for the analogous 4,5-dimethyl-1,3-dioxolanes.[10] These downfield shifts are significantly smaller than predicted on the basis of simple addition of the α- and β-effects evaluated from the mono-4-methyl-substituted derivatives. This discrepancy has been ascribed to the interaction between the vicinal methyl groups. In cyclohexanes[22] and 1,3-dioxolanes[10] this vicinal effect is reported to produce upfield shifts of approximately 3–4 ppm, of similar magnitude and direction as observed in the present compounds.

The ^{13}C methyl signals in the *cis* isomers of **9–11** appear about 2 ppm upfield of the methyl resonances of the other stereoisomers of **7–11**. This upfield shift can be largely ascribed to the sterically induced γ-effect.[12,22] The methyl substituent at C-4 or C-5 is *gauche* related to the vicinal methyl carbon, which should suffer an upfield γ-*gauche* shift effect for the *cis* isomer, as observed (there are two γ-*gauche* interactions in the *cis* isomer compared with only one for the *trans* form).

^{1}H–^{1}H coupling constants

The observed values of ^{2}J(H-A, H-B) in the C—CH_2—O moiety cover the range −8.7 to −9.2 Hz. These values are very close to those reported for a series of analogous arsolanes,[13,14] phospholanes[15,17] and ethylene sulphites.[18]

It is seen that ^{2}J(HH) in the five-membered arsenites is about 2 Hz more positive than in the six-membered 1,3,2-dioxarsenanes. This observation is general when comparing geminal coupling constants in five- and six-membered ring analogues. This effect has been ascribed to the increased possibilities of transfer of lone pairs of electrons into the antisymmetric CH_2 molecular orbitals of five-membered heterocycles.[23,24] It has been argued[23b,c] that this arises because the five-membered rings exist in conformations such that the lone electron pairs of the α-heteroatom more or less eclipse the adjacent CH bonds, in contrast to the situation in the chair conformation of six-membered rings. This conclusion is supported by molecular models of the arsolane ring.

The two *cis* coupling constants, ^{3}J(H-A, H-A′) and ^{3}J(H-B, H-B′) are practically identical in the studied dioxarsolanes (**1–5**), in accordance with the situation in dithiarsolanes,[13c] diazarsolanes,[13f] dioxaphospholanes[17,25] and ethylene sulphite.[17,18b]

The *trans* coupling constant is larger than the corresponding *cis* coupling constant in **1–5**. The same observation has been made for the dithiarsolanes,[13c] dithiaphospholanes[26,27] and dithiolanes.[28] The reverse, however, is true for the dioxaphospholanes,[6,17,25] diazaphospholanes,[29] dioxolanes[2,30] and ethylene sulphite.[17,18b] The large variation in the *cis* and *trans* coupling constants of comparable systems reflects changes in the average X—C—C—X torsional angle of these five-membered rings (X = O, N or S). The large *trans* coupling constant in the sulphur-containing

rings indicates, in particular, a higher degree of ring puckering with respect to their oxygen or nitrogen counterparts. Thus, *R*-value calculations[31] based on the present and previously reported CH_2–CH_2 coupling constants for dithiarsolanes,[13c] dithiaphospholanes,[26,27] dithiolanes,[28] dioxarsolanes,[14] dioxaphospholanes,[17,25] dioxolanes,[2,30] diazarsolanes[13f] and diazaphospholanes[29] give torsional angles of 55, 48, 49, 46, 42, 43, 46 and 41°, respectively. These figures are average values over a series of investigated compounds. It is likely that a part of the variation in the torsional angle is apparent rather than real, i.e. it is due to uncertainties in the observed coupling constants and the *R*-value method. Further, it has been pointed out that the *R*-value method consistently overestimates torsional angles in five-membered rings.[5] The general trend, however, is that the arsolane rings are more puckered than their phosphorus counterparts which, on the other hand, have similar puckering to the corresponding dioxolanes and dithiolanes. Moreover, replacement of oxygen by nitrogen in these heterocyclic rings seems to have only a small effect on the ring puckering, in contrast to sulphur, which produces a significant increase in the ring puckering.

The magnitudes of the vicinal ^3J(HH) coupling constants of the 4-methyl-1,3,2-dioxarsolanes and -1,3,2-dithiarsolanes[13d,e] support the assumption made earlier in the text that these heterocyclic rings exist in rapidly interconverting half-chair conformations such as S_1, S_2 and A_1, A_2 for the *syn* and *anti* isomers, respectively (Scheme 3). Thus, the large value of ^3J(H-A, H-C) (*ca* 10 Hz) in the *syn* forms of **7** and **8** suggests a strong predominance of S_2-like conformers where the coupled H-A and H-C protons have a *trans* relationship. Further support for this assumption is found in the similar values of ^3J(H-A, H-C) and ^3J(H-4a, H-5a) observed in the *syn* (*cis*) isomers of 4- or 5-methyl-substituted arsolanes[13d,e] and arsenanes.[19] A significant contribution of S_1-like conformers would result in a smaller value of ^3J(H-A, H-C), contrary to that found experimentally. Since the H-B proton is *trans* to the oxygen heteroatom in the S_2 conformer, a smaller value of ^3J(H-B, H-C) was expected (maximal inductive effect)[2,32] in the dioxarsolanes relative to the dithiarsolanes.[13d,e] The reverse observation indicates that the *cis* coupling constant is dominated by conformational rather than stereospecific inductive effects.

The vicinal proton coupling constants in the 4-methyl-1,3,2-dithiarsolanes,[13d,e] -1,3,2-dioxaphospholanes[6] and -1,3,2-dithiaphospholanes[33] and propylene sulphite[18b] are also consistent with a strong predominance of S_2-like conformations for the *syn* isomers. The *syn* isomers thus appear to be conformationally biased towards the form with 4-methyl pseudoequatorial. In contrast, the more similar values of the *cis* and *trans* coupling constants in the *anti* isomers indicate significant contributions from A_1- and A_2-like conformers, as expected on steric grounds.

It is interesting that the vicinal ^3J(HH) value in the *trans* molecules of **9–11** is considerably larger than the corresponding coupling in the *cis* molecules.[13a,b] The *trans* isomers, therefore, appear to be strongly biased towards the T_2-form where the coupled H-A and H-C protons have a *trans* relationship (Scheme 4). In contrast, since the coupled protons are *gauche* in the C_1 and C_2 *cis* isomers, a small vicinal coupling is observed (Scheme 4).

^{13}C–^{1}H coupling constants

The present data clearly demonstrate that the ^{13}C–^{1}H coupling constants are very sensitive to stereochemical effects. It is thus seen that the two one-bond coupling constants of the methylene group in **2–8**, ^1J(C-5, H-A) and ^1J(C-5, H-B), are distinctly different, with the largest value for the latter coupling except in **5**. The difference is particularly large for the compounds which are conformationally biased, that is, the *syn* isomers of **7** and **8**. Similar stereochemical dependences have also been observed in related five- and six-membered rings.[21,34,35] The variation in ^1J(CH) is largely ascribed to hybridization changes in the C—H bond and a stereospecific substituent effect of the adjacent heteroatom.[12,35]

Typical values of the two-bond ^{13}C–^{1}H coupling constants in aliphatic systems containing electronegative substituents range from −5 to +2 Hz.[12,35,36] The measured geminal ^{13}C–^{1}H coupling constants in the present compounds (−4.3 to +0.2 Hz) fall well within this range. It is seen that, whereas the two geminal ^{13}C–^{1}H coupling constants involving the methylene protons, ^2J(C-4, H-A) and ^2J(C-4, H-B), are nearly identical for the unsubstituted compounds **1–5**, a large variation is observed for the 4-methyl derivatives. It is noteworthy that the more positive one- and two-bond coupling constants in **6–8** always involve the C-5—H-B bond. This may reflect a higher degree of s-character of the C-5—H-B bond compared with the C-5—H-A bond, since increasing s-character of the hybrid orbitals has been reported to increase ^1J(CH) as well as ^2J(CH).[12,35]

In addition, ^2J(C-5, H-C) is significantly more positive in the *anti* isomers than in the *syn* isomers of **7** and **8** and the corresponding dithiarsolanes. This positive contribution is believed to be produced by a maximal inductive contribution of one of the oxygen atoms in the A_2 conformer (O-1 is roughly in the plane of the C-5–C-4–H-C coupling path, Scheme 3).[37] Äyräs[38] correlated ^2J(CH_3, H) in five- and six-membered rings with the corresponding ^2J(HH) coupling constant to give the relationship

$$^2J(CH_3, H) = 0.55\ ^2J(HH) + 4.93 \qquad (1)$$

The geminal ^{1}H–^{1}H coupling constants in the present compounds are practically constant, with an average value of −8.96 Hz. By using this value, Eqn (1) predicts that ^2J(CH_3, H) is close to zero, as observed.

It is interesting that the difference between the two ^3J(CH_3, H) vicinal coupling constants in **7** and **8** is much larger in the *syn* than in the *anti* isomers. This observation can be rationalized on the basis of a Karplus-like dihedral angle dependence[12,39] and a stereospecific inductive effect of the oxygen heteroatoms.[12,37,40] Specifically, the small value of ^3J(CH_3, H-B) in the *syn* isomers is doubtless the result of a maximal inductive effect of the O-3 heteroatom,

which is situated roughly in the plane of the C-4–C-5–H-B coupling path of the S_2 conformer (Scheme 3). In the *anti* isomers, however, the oxygen atoms affect the two $^3J(CH_3, H)$ coupling constants to a more similar extent, since both pseudo-conformers contribute. The large value of $^3J(CH_3, H\text{-}B)$ is therefore attributed to a significant contribution from A_2 where the methyl carbon and H-B have the favourable *trans* relationship (Scheme 3).

Similarly, the large values of the $^3J(CH_3, H)$ coupling constants in the *trans* isomers of **9–11** indicate a predominance of the T_2 conformer, in which the oxygen atoms are situated well off the $^{13}C–C–^1H$ coupling paths and hardly affect the coupling constants (Scheme 4). In the *cis* isomers, however, the average $^3J(CH_3, H\text{-}A)$ coupling constant is considerably reduced by the inductive effect, since one of the oxygen atoms has a more favourable orientation with respect to the coupling path (Scheme 4).

EXPERIMENTAL

The syntheses of the 2-chloro-1,3,2-dioxarsolanes (**1**, **6** and **9**) have been described in previous papers.[13] The 2-methoxy, 2-phenoxy, 2-methylthio and 2-phenylthio compounds were prepared from the appropriate chloro compounds and methanol, phenol, methyl mercaptan and thiophenol, in diethyl ether using triethylamine as base.

The NMR samples of the freshly distilled compounds were recorded in 30% v/v benzene-d_6 solutions. The solutions were transferred to 5 and 10 mm o.d. NMR tubes, degassed by freeze–pump–thaw cycles, filled with nitrogen and sealed.

The 90 MHz ^1H and 22.63 MHz ^{13}C NMR spectra were obtained at ambient probe temperature (*ca* 30 °C) on a Bruker CXP 100 spectrometer. The 100.62 MHz ^{13}C spectra of **6**, **7** and **8** were run on a Bruker WM-400 spectrometer. Gated decoupling with a duty cycle of 6 s was used to give a fully coupled ^{13}C spectrum while retaining the nuclear Overhauser enhancement factor.

The spectral windows of the ^{13}C spectra were carefully chosen to ensure that folding did not obscure the spectral region of interest, while at the same time giving a digital resolution of 0.15 Hz or better for the 22.63 MHz spectra. Gaussian multiplication or exponential weighting were applied to the 16K free induction decays.

The ^1H and ^{13}C chemical shifts were measured with respect to internal TMS and benzene-d_6, respectively, by use of extended spectral windows.

The ^1H and ^{13}C spectra were analysed by means of the LACX,[41] LAOCN3,[42] UEAITR[43] and KOMBIP[44] computer programs. The computations were performed on a Univac 1100/32 computer and the graphical output was obtained using a Calcomp 1051 plotter.

REFERENCES

1. C. Altona, H. R. Buys and E. Havinga, *Recl. Trav. Chim. Pays-Bas* **85,** 973 (1966).
2. H. Booth, *Prog. Nucl. Magn. Reson. Spectrosc.*, edited by J. W. Emsley, J. Feeney and L. H. Sutcliffe, Pergamon Press, Oxford, **5,** 149 (1969).
3. W. E. Willy, G. Binsch and E. L. Eliel, *J. Am. Chem. Soc.* **92,** 5394 (1970).
4. G. E. Wilson, Jr., *J. Am. Chem. Soc.* **96,** 2426 (1974).
5. J. B. Lambert, J. J. Papay, S. A. Kahn, K. A. Kappauf and E. Stedman Magyar, *J. Am. Chem. Soc.* **96,** 6112 (1974).
6. W. G. Bentrude and H.-W. Tan, *J. Am. Chem. Soc.* **98,** 1850 (1976).
7. E. L. Eliel, *J. Chem. Educ.*, **52,** 762 (1975).
8. V. F. Bystrov, *Prog. Nucl. Magn. Reson. Spectrosc.*, edited by J. W. Emsley, J. Feeney and L. H. Sutcliffe, Pergamon Press, Oxford, **10,** 41 (1976).
9. R. Benassi, L. Schenetti, F. Taddei, L. Villa and V. Ferri, *Org. Magn. Reson.* **13,** 17 (1980).
10. E. L. Eliel, V. S. Rao and K. M. Pietrusiewicz, *Org. Magn. Reson.* **12,** 461 (1979).
11. D. Besserre and S. Coffi-Nketsia, *Org. Magn. Reson.* **13,** 235 (1980).
12. (a) P. D. Ellis and R. Ditchfield, in *Topics in Carbon-13 NMR Spectroscopy*, edited by G. C. Levy, Vol. 2, p. 433. Wiley–Interscience, New York (1974); (b) F. W. Wehrli and T. Wirthlin, *Interpretation of Carbon-13 NMR Spectra*. Heyden, London (1978); (c) E. Breitmaier and W. Voelter, *^{13}C NMR Spectroscopy*. Verlag Chemie, Weinheim (1978).
13. (a) D. W. Aksnes and O. Vikane, *Acta Chem. Scand.* **26,** 835 (1972); (b) D. W. Aksnes and O. Vikane, *Acta Chem. Scand.* **26,** 2532 (1972); (c) D. W. Aksnes and O. Vikane, *Acta Chem. Scand.* **27,** 1337 (1973); (d) D. W. Aksnes and O. Vikane, *Acta Chem. Scand.* **27,** 2135 (1973); (e) D. W. Aksnes and M. Bjorøy, *Acta Chem. Scand., Ser. A* **29,** 672 (1975); (f) D. W. Aksnes, F. A. Amer and K. Bergesen, *Acta Chem. Scand., Ser. A* **30,** 109 (1976).
14. O. Adler and F. Kober, *Monatsh. Chem.* **108,** 65 (1977).
15. K. Bergesen and T. Vikane, *Acta Chem. Scand.* **26,** 2153 (1972).
16. H.-W. Tan and W. G. Bentrude, *Tetrahedron Lett.* 619 (1975).
17. P. Haake, J. P. McNeal and E. J. Goldsmith, *J. Am. Chem. Soc.* **90,** 715 (1968).
18. (a) C. H. Green and D. G. Hellier, *J. Chem. Soc., Perkin Trans 2* 1966 (1973); (b) C. H. Green and D. G. Hellier, *J. Chem. Soc., Perkin Trans. 2* 243 (1973); (c) C. H. Green and D. G. Hellier, *J. Chem. Soc., Perkin Trans. 2* 190 (1975).
19. (a) D. W. Aksnes, J. Andersen and K. Bergesen, *Acta Chem. Scand., Ser. A* **30,** 327 (1976); (b) D. W. Aksnes, K. Bergesen and O. Strömme, *Acta Chem. Scand., Ser. A* **33,** 413 (1979).
20. D. Tavernier and M. Anteunis, *J. Magn. Reson.* **13,** 181 (1974).
21. D. W. Aksnes and T. A. Holak, *Org. Magn. Reson.* **18,** 28 (1982).
22. D. K. Dalling and D. M. Grant, *J. Am. Chem. Soc.* **94,** 5318 (1972).
23. (a) R. C. Cookson, T. A. Crabb, J. J. Frankel and J. Hudec, *Tetrahedron, Suppl.* **7,** 355 (1966); (b) R. Cahill, R. C. Cookson and T. A. Crabb, *Tetrahedron* **25,** 4681 (1969); (c) R. Cahill, R. C. Cookson and T. A. Crabb, *Tetrahedron* **25,** 4711 (1969).
24. J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.* **42,** 1339 (1965).
25. D. Gagnaire, J. B. Robert, J. Verrier and R. Wolf, *Bull. Soc. Chim. Fr.*, 3719 (1966).
26. S. C. Peake, M. Fild, R. Schmutzler, R. K. Harris, J. M. Nichols and R. G. Rees, *J. Chem. Soc., Perkin Trans. 2* 380 (1972).
27. K. Bergesen, M. Bjorøy and T. Gramstad, *Acta Chem. Scand.* **26,** 2156 (1972).
28. L. A. Sternson, D. A. Coviello and R. S. Egan, *J. Am. Chem. Soc.* **93,** 6529 (1971).
29. J. P. Albrand, A. Cogne, D. Gagnaire and J. B. Robert, *Tetrahedron* **28,** 819 (1972).

30. C. Altona and A. P. M. van der Veek, *Tetrahedron* **24,** 4377 (1968).
31. J. B. Lambert, *Acc. Chem. Res.* **4,** 87 (1971).
32. D. H. Williams and N. S. Bhacca, *J. Am. Chem. Soc.* **86,** 2742 (1964).
33. (a) K. Bergesen and M. Bjorøy, *Acta Chem. Scand.* **27,** 1103 (1973); (b) K. Bergesen and M. Bjorøy, *Acta Chem. Scand.* **27,** 3477 (1973).
34. D. W. Aksnes and O. Strömme, *Acta Chem. Scand., Ser. A* **35,** 617 (1981).
35. P. E. Hansen, *Prog. Nucl. Magn. Reson. Spectrosc.*, edited by J. W. Emsley, J. Feeney and L. H. Sutcliffe, Pergamon Press, Oxford, **14,** 175 (1981).
36. D. F. Ewing, *Ann. Rep. NMR Spectrosc.*, edited by E. F Mooney, Academic Press, London, **6A,** 389 (1975).
37. F. J. Weigert and J. D. Roberts, *J. Phys. Chem.* **73,** 449 (1969).
38. P. Äyräs, *Acta Chem. Scand., Ser. B* **31,** 325 (1977).
39. (a) M. Barfield, *J. Am. Chem. Soc.* **102,** 1 (1980); (b) M. Barfield, *J. Am. Chem. Soc.* **102,** 7 (1980).
40. T. Spoormaker and M. J. A. de Bie, *Recl. J. R. Neth. Chem. Soc.* **99,** 154 (1980).
41. C. W. Haigh, *LACX*, Department of Chemistry, University College, Swansea, Wales.
42. A. A. Bothner-By and S. Castellano, *QCPE Program 111*, Quantum Chemistry Program Exchange, Indiana University (1974).
43. R. B. Johannesen, J. A. Ferretti and R. K. Harris, *J. Magn. Reson.* **3,** 84 (1970).
44. D. W. Aksnes, *QCPE Program 205*, Quantum Chemistry Program Exchange, Indiana University (1974).

Received 16 November 1982; accepted (revised) 24 January 1983