Naphthalene Tetrachlorides and Related Compounds. Part 10.[1] The Carbon-13 Nuclear Magnetic Resonance Spectra of Some Naphthalene Tetrachlorides

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Details of the carbon-13 n.m.r. spectra of four 1,2,3,4-tetrachlorotetralins (naphthalene tetrachlorides) and of three 1,2,3,4-tetrachloro-2-methyltetralins are presented. Chemical shifts of the signals attributable to the individual alicyclic and aromatic carbon atoms have been recorded and as far as possible identified by conventional methods; $^1J_{C,H}$ coupling constants have also been recorded. Several different types of $^2J_{C,H}$ and $^3J_{C,H}$ coupling constants have been identified from the details of the single resonance and partly decoupled high-resolution spectra. The results are discussed in relation to the known stereochemistry of these compounds.

ELSEWHERE [2-4] ^{1}H n.m.r. spectroscopy has been used in conjunction with other techniques [5,6] to define the stereochemistry of the five known naphthalene tetrachlorides. Of these, the four whose structures are shown in diagrams (1)—(4) were available to us in quantity sufficient for useful determination of their ^{13}C n.m.r. spectra. Results from the use of this technique were expected to be helpful in extending knowledge of the factors determining chemical shifts and coupling constants in compounds of defined geometry; relatively few values of long-range ($^2J_{C,H}$ and $^3J_{C,H}$) coupling constants are available in the literature.[7,8] The comparisons are extended by inclusion of values for the three 2-methylnaphthalene tetrachlorides (5)—(7).[1]

EXPERIMENTAL

Both ^{1}H and ^{13}C spectra were determined by using a JEOL FX60 spectrometer. Fully decoupled ^{13}C spectra, single resonance ^{13}C spectra with nuclear Overhauser enhancement, and ^{13}C spectra specifically decoupled by irradiation at the frequencies of signals attributable to particular protons or groups of protons in the ^{1}H spectrum were recorded. The solvent was $CDCl_3$ for measurement of chemical shifts; for measurement of coupling constants in the undecoupled spectra, 1,1,2,2-tetrachloroethane was sometimes used to give greater solubility. Chemical shifts are recorded as p.p.m. downfield from tetramethylsilane used as internal reference. Coupling constants are in Hz; the instrumentation allowed accuracy of ±0.3 Hz. Details of some of the spectra are given in the Supplementary Publication No. 23056 (24 pp.).† The compounds used were samples prepared in the course of earlier studies; [1-4] they were, respectively, the naphthalene α-, γ-, δ-, and ε-tetrachlorides, *viz.* the *r*-1,*c*-2,*t*-3,*t*-4-; *r*-1,*t*-2,*c*-3,*t*-4-; *r*-1,*c*-2,*t*-3,*c*-4-; and *r*-1,*t*-2,*t*-3,*c*-4-tetrachlorotetralins (1)—(4), and the related *r*-1,*c*-2,*t*-3,*t*-4-, *r*-1,*t*-2,*c*-3,*t*-4-, and *r*-1,*c*-2,*t*-3,*c*-4-tetrachloro-2-methyltetralins (5)—(7). Estimates of dihedral angles have been made by examination of appropriate models; they neglect distortions resulting from intramolecular and other non-bonding forces. For (1)—(3) and (5)—(7) the structures given imply also the presence in equal quantity of the enantiomer.

The naphthalene tetrachloride (4) is a *meso*-form, and conformational equilibrium makes C-1 and -4 equivalent, as are C-2 and -3; the ^{1}H n.m.r. spectrum [2] establishes that this isomerisation is rapid. Conformational isomerisation should be rapid for the other compounds also. On the basis that the conformers can be assumed to have idealised geometry, the coupling constants in the ^{1}H n.m.r. spectra can be used to calculate the proportions rounded off to the nearest 10% as in a previous paper,[3] namely (1a), *ca.* 90%; (2a), *ca.* 70%; (3a), 70—90% (the mean value is adopted); and (7a), *ca.* 80%. On the same basis, (6a) also comprises *ca.* 80% of its equilibrium between conformers. No similar estimate can be made for (5b), because the values of $J_{3,4}$ would here be nearly the same in both conformations, but for the reasons given in Part 9,[1] it is assumed that this comprises at least 80% of the equilibrium mixture of conformers, and this value has been assumed for the purpose of the derived computations. The basis for these estimates is that reductions of the coupling constants below the maxima expected from the Karplus relationship [9] occur because of the coexistence of two conformational isomers. This approach has been used in an earlier paper in this series [3] and by others; [10] but it will be seen that another type of explanation needs to be considered as possibly contributing to these reductions for the present series of compounds.

RESULTS

The chemical shifts of the signals attributable to the individual carbon atoms in the ^{13}C spectra of the isomeric naphthalene tetrachlorides are recorded in Table 1, together with values of the major coupling constants ($^1J_{C,H}$) obtained from the spacings of the doublets identifiable as signals for the protonated carbon atoms in the undecoupled ^{13}C spectra. Most of the latter values could be estimated within the precision of the measurements (±0.3 Hz); the aromatic signals, however, were complicated overlapping multiplets having slightly different major spacings, and so the coupling constants are reported with rather less precision. Values of chemical shifts refer to results obtained in $CDCl_3$ as solvent with tetramethylsilane as reference except where otherwise noted. Small changes in the values were noted when $(CD_3)_2CO$ was used as solvent.

The signals were assigned by means of their chemical shifts and coupling constants; and where necessary by means of spin-decoupling experiments, which were used also to assign some of the coupling constants. Details are given in the SUP 23056.

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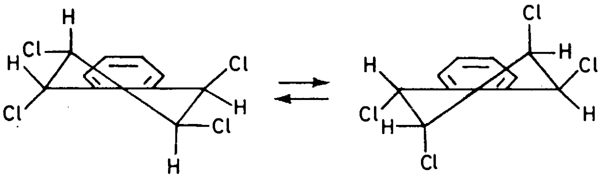
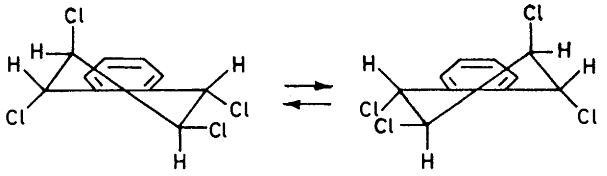
† For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1980, Index issue.



(1a) (1b)

Main conformation
in solution; *ca*. 90 %

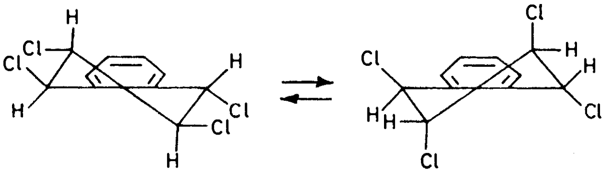
naphthalene α-tetrachloride



(4a)
(50%)

(4b)
(50%)

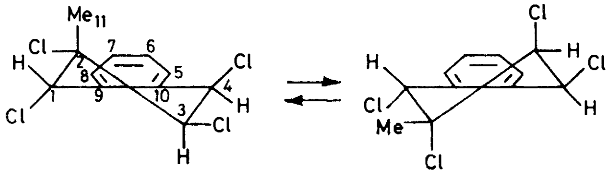
naphthalene ε-tetrachloride



(2a) (2b)

Main conformation
in solution; *ca*. 70 %

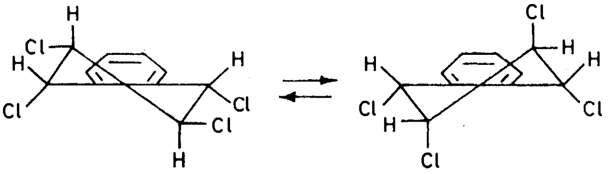
naphthalene γ-tetrachloride



(5a) (5b)

Main conformation in
solution; assumed *ca*. 80 %

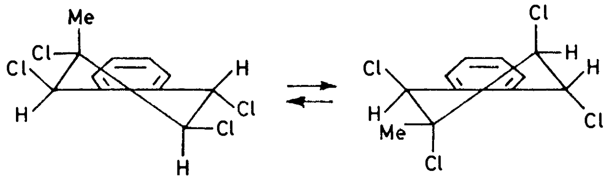
2-methylnaphthalene α-tetrachloride (oil)



(3a) (3b)

Main conformation
in solution; *ca*. 80 %

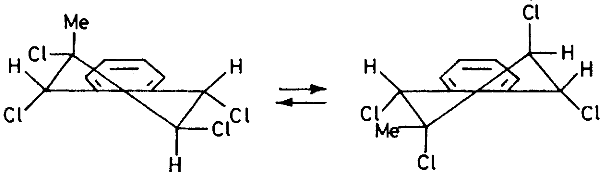
naphthalene δ-tetrachloride



(6a) (6b)

Main conformation
in solution; *ca*. 80 %

2-methylnaphthalene γ-tetrachloride (m.p. 135·5°)



(7a) (7b)

Main conformation
in solution; *ca*. 80 %

2-methylnaphthalene δ-tetrachloride (m.p. 99°)

The values of long-range ($^{2}J_{\mathrm{C,H}}$, $^{3}J_{\mathrm{C,H}}$) constants estimated from the multiplicity and spacings of identifiable signals for the alicyclic carbon atoms in the single-resonance spectra of the tetrachlorides are given in Table 2. Good agreement between estimates made separately on the individual halves of the doublets split by the major ($^{1}J_{\mathrm{C,H}}$) coupling was obtained where this feature was not obscured by overlapping of signals. Many of the expected couplings which obviously were present were not able to be estimated with useful accuracy.

TABLE 1

Chemical shifts (p.p.m. downfield from Me_4Si) and (in parentheses) coupling constants ($^1J_{C,H}$/Hz) in the ^{13}C n.m.r. spectra of four naphthalene tetrachlorides and three 2-methylnaphthalene tetrachlorides

Tetrachloride		C-1	C-2	C-3	C-4	C-5	C-8	C-6	C-7	C-9	C-10	C-11
2-H; (1)	(α)	61.81 (158.7)	59.47 (152.6)	59.47 (152.6)	61.81 (158.7)	129.86 (162)	129.86 (162)	129.86 (162)	129.86 (162)	132.98	132.98	
2-H; (2)	(γ)	61.76 (157.5)	65.90 (161.1)	65.90 (161.1)	61.76 (157.5)	128.69 (163)	128.69 (163)	129.24 (163)	129.24 (163)	132.66	132.66	
2-H; (3)	(δ)	61.68 (159.9)	61.55 (153.8)	64.09 (162.0)	62.98 (155.0)	128.63 (163)	129.41 (163)	129.93 (163)	130.19 (163)	132.85	133.17	
2-H; (4)	(ϵ)	59.60 (158.1)	61.94 (159.9)	61.94 (159.9)	59.60 (158.1)	130.06 (162)	130.06 (162)	129.60 (162)	129.60 (162)	132.13	132.13	
2-Me; (5)	(α)	63.31 (*ca.* 155)	72.97	68.75 (163)	58.31 (154)	128.9 * (162)	128.9 *	128.6 *	128.9 *	131.2 †	132.5 †	29.18 (130.6)
2-Me; (6) [$(CD_3)_2CO$ solvent]	(γ)	69.12 (157.2)	74.57	72.20 (160.2)	63.76 (157.7)	129.2 * (163)	129.8 *	130.0 *	130.4 *	133.6 †	133.8 †	18.80 (130.5)
2-Me; (7) [$(CD_3)_2CO$ solvent]	(δ)	67.62 (159.7)	72.10	69.41 (160.2)	63.11 (157.2)	129.5 * (161)	130.0 *	130.3 *	130.5 *	133.0 †	133.2 †	23.47 (130.9)

* Assignments arbitrary. † Assignments can be reversed.

TABLE 2

Long-range coupling constants involving signals for the non-aromatic carbon atoms in the ^{13}C n.m.r. spectra of four naphthalene tetrachlorides and three 2-methylnaphthalene tetrachlorides

Compound	(1)	(2)	(3)	(4)	(5)	(6)	(7)
2-Substituent	H	H	H	H	Me	Me	Me
Structural type *	α	γ	δ	ϵ	α	γ	δ
$^2J_{C-1,H-2}$/Hz	2.4	NR	NR	2.0	Abs †	Abs	Abs
$^2J_{C-2,H-1}$/Hz	3.1	5.5	6.1	5.5	NR ‡	NR	NR
$^2J_{C-2,H-3}$/Hz	5.5	6.7	4.3	1.2	NR	NR	NR
$^2J_{C-3,H-2}$/Hz	≡5.5	≡6.7	6.7	≡1.2	Abs	Abs	Abs
$^2J_{C-3,H-4}$/Hz	≡3.1	≡5.5	6.7	≡5.5	Small	7.0	6.6
$^2J_{C-4,H-3}$/Hz	≡2.4	NR	NR	≡2.0	4.8	6.1	6.8
$^3J_{C-1,H-3}$/Hz	2.4	NR	NR	5.0	5.0	1.5	2.1
$^3J_{C-4,H-2}$/Hz	≡2.4	NR	NR	≡5.0	Abs	Abs	Abs
$^3J_{C-2,H-4}$/Hz	5.5	2.4	Small	3.7	NR	NR	NR
$^3J_{C-3,H-1}$/Hz	≡5.5	≡2.4	6.7	≡3.7	small	1.5	6.6
$^3J_{C-1,H-11}$/Hz	Abs	Abs	Abs	Abs	NR	3.4	5.4
$^3J_{C-3,H-11}$/Hz	Abs	Abs	Abs	Abs	4.3	3.9	3.4
$^3J_{C-11,H-1}$/Hz	Abs	Abs	Abs	Abs	2.2	4.0	2.0
$^3J_{C-11,H-3}$/Hz	Abs	Abs	Abs	Abs	2.2	4.0	4.3
$^3J_{C-1,H-8}$/Hz	NR	NR	NR	NR	5.0	4.5	NR
$^3J_{C-4,H-5}$/Hz	NR	NR	NR	NR	4.8	4.9	4.3

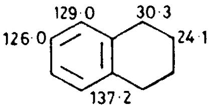
* Substituent chlorines. † Abs = Absent. ‡ NR = Not resolved. ≡ Equivalent by symmetry to a value already given.

DISCUSSION

(a) ^1H *N.M.R. Spectra of the Tetrachlorides*.—These have already been reported,[2-4] and the measurements made in the course of this work are in satisfactory agreement. We have assumed for the purpose of discussion that the estimates of the proportions of the conformers present in solutions of (1)—(3) given alongside the appropriate diagrams have been estimated with sufficient accuracy by using the observed coupling constants and Karplus-type [9] curve as in the earlier study.[3] Distortion of the molecule [*e.g.* of (2)] by internal compression might, however, affect any estimate made in this way, and the exact values should be treated with some reserve.

(b) *Chemical Shifts for Signals in the* ^{13}C *Spectra*.—One basis which can be used for discussion of the values for the chemical shifts of the signals for carbon atoms in the ^{13}C spectra of the naphthalene tetrachlorides involves comparison with the values for tetralin (8), modified where necessary by the empirical parameters for calculation of chemical shifts in cyclohexanes tabulated by Wehrli and Wirthlin.[8]

Values of the chemical shifts shown are in units of δ (p.p.m. downfield from Me_4Si). Considering first the aromatic signals in the ^{13}C spectra of the naphthalene tetrachlorides (Table 1), these vary only a little with the stereochemistry of substitution in the alicyclic ring. The values can be interpreted in terms of known analogies. The values for C-6 and -7 are shifted downfield by 4—5 p.p.m., probably because of the inductive effect of the chlorine substituent,[11,12] and the values of C-5 and -8, having no doubt been shifted downfield for a similar reason, are shifted back upfield by steric compression [11,12] around these centres caused by the closeness of the large substituents on C-1. The values for C-9 and -10 are downfield from their position in benzene because of the



(8)

additional substitution, but are upfield from tetralin probably again because of steric compression.

Calculated chemical shifts for the alicyclic carbon atoms on the basis that these will be modified from the values for tetralin by the empirical parameters appropriate to chlorine substituents in cyclohexane systems are given in Table 3. It can be seen that all the signals lie upfield from the calculated values by 10.6 ± 2 units of δ. The additional shielding can probably be attributed to the general congestion of the polysubstituted system.

Table 3

Calculated chemical shifts δ (p.p.m. downfield from Me_4Si) and chemical shift differences ($\Delta = \delta^{found} - \delta^{calc}$) for the signals of the alicyclic carbon atoms in four naphthalene tetrachlorides

	δ^{calc} (p.p.m. from Me_4Si) *				$\Delta = \delta^{found} - \delta^{calc}$			
Compound	C-1	C-2	C-3	C-4	C-1	C-2	C-3	C-4
2-H; (1a) (α)	73.3	69.1			−11.5	−9.6		
2-H; (2a) (γ)	72.3	79.1			−10.5	−13.2		
2-H; (3a) (δ)	72.3	75.1	73.1	73.3	−10.4	−13.5	−9.0	−10.3
2-H; (4a,b) (ε)	67.8	72.1			−8.2	−10.2		

* Illustrative calculation (see text): (1a), C-1: 30.3 (tetralin) + 33.0 (Cl_α) + 11.0 (Cl_β) + 0.0 (Cl_γ) − 1.0 (Cl_δ) = 73.3.

For discussion of the influence of the 2-methyl group on the chemical shifts of the alicyclic carbon atoms, it seems best to make comparison directly with the values for the corresponding naphthalene tetrachlorides. The results are given in Table 4.

Considering first the two cases in which introduction of a methyl group does not result in conformational change, similar patterns of change of chemical shift are observed; the signals for C-2, α to the new substituent, are moved substantially downfield, and so are those for the two β-carbon atoms, C-1 and -3. The signals for the γ-carbon atoms, C-4, are not much changed in position. The results for β-carbon atoms accord with what would be expected on the basis of the tabulated [8] empirical parameters; but those for the attached and for the γ-carbon atom are very different, lying 6—11 units of δ further downfield. Clearly the combined effects of methyl and chlorine substituents are either not additive, or not transferable from a cyclohexane to a benzocyclohexene system, even for substituents on the cyclohexane-like carbon atom C-2.

Table 4

Change in ^{13}C chemical shift δ of alicyclic carbon atoms (p.p.m. downfield from Me_4Si) resulting from the introduction of a methyl substituent into the 2-position in the naphthalene tetrachlorides (1)—(3)

Carbon atom	C-1	C-2	C-3	C-4
δ(5)–δ(1) *	1.5	13.5	9.3	−3.5
δ(6)–δ(2)	7.4 †	8.7 ‡	6.3 †	2.0 §
δ(7)–δ(3)	5.8 †	10.6 ‡	5.3 †	0.1 §

* Conformational change as well as substituent change. † Empirical parameter [8] for an axial methyl group β to the relevant carbon atom, +5.4. ‡ Empirical parameter [8] for an axial methyl group α to the relevant carbon atom, +1.4. § Empirical parameter [8] for an axial methyl group γ to the relevant carbon atom, −6.4.

The pattern of change in chemical shift when the introduced methyl group produces a change in conformation of the alicyclic ring is notably different, particularly in that the signal for C-1 is not markedly changed in position by the combined changes. In our view this result supports the configurational assignments made for these compounds; beyond this, we do not think that the structural influences can be usefully analysed in detail, though it can be noted that, as for the cyclohexanes, an equatorial methyl group appears to produce a greater downfield effect than an axial methyl group on the position of the signal for the attached carbon atom.

The chemical shifts for the methyl substituent fall within the range (δ 17—34) normal for methyl-substituted cyclohexanes; but the signal for the equatorial methyl group in (5) is shifted further downfield (δ 29.2) than those for the axial methyl groups (δ 18.8, 23.5), in accordance with the difference observed in the cyclohexane series.

(c) *Values of* $^1J_{C,H}$ (*Table* 1).—All the values of $^1J_{C,H}$ for protonated aromatic carbon atoms lie in the region 161—163 Hz. The corresponding value for benzene [13] is 159 Hz; for mesitylene, it is 154 Hz, so it seems likely that the electronegativity of the substituents in the ring has a small influence on the couplings.

The values for the alicyclic carbon atoms are in the range 152—163 Hz, much higher than the value in cyclohexane (126.4 for H_e, 122.4 Hz for H_a),[7] presumably because of the electronegativity of the substituents.[14] A similarly high value (160.3 Hz) has been recorded for β-benzene hexachloride,[15] in which all the hydrogen atoms are axial. Factors other than the orientation of the proton, or of the directly attached substituent, obviously are concerned in determining the variation in $^1J_{C,H}$ for the tetrachlorides examined in the present investigation, since for example, $^1J_{C\text{-}3,H}$ for (1) is 152.6 Hz and for (3) is 162.0 Hz, both these protons being axial. The results suggest that the influence of an adjacent electron-withdrawing substituent on $^1J_{C,H}$ is at a minimum when the proton is axial or pseudo-axial and the substituent is likewise axial or pseudo-axial, since in the compounds under investigation only the C–H bonds having an *anti*-chlorine axial or pseudo-axial have relatively small couplings ($^1J_{C,H}$) for C-1 in (5), *ca.* 155 Hz; for C-4 in (5), 154 Hz; for C-2 and -3 in (1), 152.6 Hz; for C-2 and -3 in (3), 153.8 Hz.

The values of $^1J_{C\text{-}11,H}$ are all *ca.* 130 Hz, which is fairly normal for this substituent; the value for ethane [16] is 125 Hz.

(d) *Values of* $^2J_{C,H}$ (*Table* 2 *and Text*).—In cyclohexane, $^2J_{C,H}$ has been shown [7] to take the values -3.7 (^{13}C–C–^1H_e) and -3.9 Hz (^{13}C–C–^1H_a), being thus insensitive to the disposition of the proton with respect to the ring. Our measurements include a number of estimates of this quantity, and they vary over a wide range of numerical values; the signs of the coupling constants have not been determined. Couplings from a benzylic (H-1 or -4) proton would seem to have reasonably high values (range 3.1—7 Hz). Couplings from an alicyclic (H-2 or -3) proton cover the range 1.2—6.7 Hz. We have not been able to discern any systematic pattern dependent on the geometry of the coupled nuclei or of attached groups.

(e) *Values of* $^3J_{C,H}$ (*Table* 2 *and Text*).—In cyclohexane, values of $^3J_{C,H}$ have been shown [7] to be ^3J(^{13}C–C–C–^1H_e), 8.1; (^{13}C–C–C–^1H_a), 2.1 Hz. These have the expected angular dependence, and it has been noted that they are fitted satisfactorily by a Karplus-type equation [*e.g.* equation (1)] with A 8.1 and B 0.

$$^3J_{C,H} = A\cos^2\phi + B \qquad (1)$$

In β-benzene hexachloride,[15] $^3J_{C,H}$ has been claimed to have the value 1.2 Hz. This is lower than would be expected from equation (1), for which with A 8.1 and ϕ 60°, a value of 2.0 Hz would have been predicted. It might have been presumed that, as for $^3J_{H,H}$, the introduction of chlorine substituents could reduce the constant A in the Karplus equation.[17]

In Table 5 we follow the precedent of our earlier paper,[3] and compare the observed coupling constants with those calculated by using a two-branched Karplus-type curve, $J = 6.7\cos^2\phi$ (ϕ 90—180°); $J = 4.5\cos^2\phi$ (ϕ 0—90°). Here the value of $J_{180°}$ has been multiplied by a factor of 0.83 relative to that for cyclohexane to allow for the effect of the electronegative chlorine substituents; and the value of $J_{0°}$ has been assumed to have the same ratio to $J_{180°}$ as in the $^3J_{H,H}$ Karplus curve which we considered to be appropriate in this series. Angles (ϕ) have been estimated approximately from scale models. Very similar results were obtained by using the alternative form of the Karplus equation, $J = 2.8 - 1.1\cos\phi + 2.8\cos2\phi$.

TABLE 5

Observed ($^3J_{obs}$/Hz) and calculated ($^3J_{calc}$/Hz) values of long-range coupling constants in the ^{13}C n.m.r. spectra of some naphthalene tetrachlorides and 2-methylnaphthalene tetrachlorides

Compound	Coupling	Dihedral angle between relevant bonds (°)	$^3J_{calc}$/Hz	$^3J_{obs}$/Hz
(1)	$^3J_{C-1,H-3}$ ($\equiv {}^3J_{C-4,H-2}$)	50 (90%) 170 (10%)	2.3	2.4
(4)	$^3J_{C-1,H-3}$ ($\equiv {}^3J_{C-4,H-2}$)	170 (50%) 70 (50%)	4.5	5.0 *
(5)	$^3J_{C-1,H-3}$	70 (20%) 170 (80%)	5.3	5.0
(6)	$^3J_{C-1,H-3}$	70 (80%) 170 (20%)	1.7	1.5
(7)	$^3J_{C-1,H-3}$	50 (80%) 170 (20%)	2.8 (small)	2.1
(1)	$^3J_{C-2,H-4}$ ($\equiv {}^3J_{C-3,H-1}$)	170 (90%) 70 (10%)	5.9	5.5 *
(2)	$^3J_{C-2,H-4}$ ($\equiv {}^3J_{C-3,H-1}$)	70 (70%) 170 (30%)	2.3	2.4 *
(3)	$^3J_{C-2,H-4}$	70 (80%) 170 (20%)	1.7 (0.1)	Small
(3)	$^3J_{C-3,H-1}$	170 (80%) 70 (20%)	5.3 (6.7)	6.7
(4)	$^3J_{C-2,H-4}$	170 (50%) 70 (50%)	3.5	3.7 *
(5)	$^3J_{C-3,H-1}$	170 (20%) 70 (80%)	1.7	Small
(6)	$^3J_{C-3,H-1}$	70 (80%) 170 (20%)	1.7	1.5
(7)	$^3J_{C-3,H-1}$	170 (80%) 70 (20%)	5.3 (6.7)	6.6

* Assigned from the Karplus equation; see text.

For most of the couplings, a satisfactory fit is obtained. The largest observed value is 6.7, and others cover most of the expected range. Agreement between observed and calculated values for the δ-tetrachloride (3) would be improved if this isomer is not a mixture of conformers, but is instead exclusively in conformation (3a), slightly distorted to relieve compression between the pseudo-equatorial 4-chlorine and the 5-hydrogen atom. Inspection of a model shows that such a distortion might make ϕ quite near to 80° for $^3J_{C-2,H-4}$ and to 180° for $^3J_{C-3,H-1}$, giving the calculated results shown in parentheses. A similar distortion would be expected in the stereochemically analogous 2-methylnaphthalene tetrachloride (7), in this compound relieving also the interaction between the methyl group and C-4, and would again allow better agreement between observed and calculated values of $^3J_{C-3,H-1}$.

TABLE 6

Observed ($^3J_{obs}$/Hz) and calculated ($^3J_{calc}$/Hz) values of long-range couplings involving the methyl groups in the ^{13}C n.m.r. spectra of some 2-methylnaphthalene tetrachlorides

Compound	Coupling	ϕ (°)	$^3J_{calc}$/Hz	$^3J_{obs}$/Hz
(5)	$^3J_{C-11, H-1}$	50 (both conformations)	1.9	2.2
(6)	$^3J_{C-11, H-1}$	170 (80%) 50 (20%)	5.8	4.0
(7)	$^3J_{C-11, H-1}$	50 (both conformations)	1.9	2.0
(5)	$^3J_{C-11, H-8}$	50 (80%) 180 (20%)	2.8	2.2
(6)	$^3J_{C-11, H-3}$	180 (80%) 50 (20%)	5.7	4.0
(7)	$^3J_{C-11, H-3}$	180 (80%) 50 (20%)	5.7	4.3
(6)	$^3J_{C-1, H-11}$	Average *	2.8	3.4
(7)	$^3J_{C-1, H-11}$	Average *	2.8	5.4
(5)	$^3J_{C-3, H-11}$	Average *	2.8	4.3
(6)	$^3J_{C-3, H-11}$	Average *	2.8	3.9
(7)	$^3J_{C-3, H-11}$	Average *	2.8	3.5

* See text.

Observed couplings in (5)—(7) between H-1 and -3 and the methyl carbon atoms also accord quite reasonably with the same treatment, as is shown in Table 6. Distortions in (7) which might affect the ring-angles would not so greatly influence the angles subtended with the methyl group, though the agreement between observed and calculated values would even so probably be improved by this type of assumption, observed values tending to be somewhat lower than those calculated.

Contrasting with this, the observed couplings between the methyl protons and the carbon atoms C-1 and -3 are consistently higher than the calculated values, which have been derived on the basis that the methyl groups are rotating freely so that averaged couplings are measured. The explanation is probably that these protons are less affected by the electronegativity of the chlorine atoms, which is known to reduce the constants in the Karplus equation. The largest discrepancy is in fact for $^3J_{C-1,H-11}$ in the tetrachloride (7), where the methyl protons lie on an axial substituent and only the 2- and 3-chlorine atoms are close.

Values of three-bond couplings between C-1 or -4 and the *peri*-hydrogen atoms H-8 or -5 are recorded also for the 2-methylnaphthalene tetrachlorides in Table 2. They all lie in the range 4.3—5 Hz; it would not necessarily be expected that the coupling $^1H-C_{Ar}-C_{Ar}-^{13}C$ would have the same value as that for $^1H-CR_2-CR_2-^{13}C$ held at a dihedral angle of 0°, but it is worth noting that the Karplus curve which we have regarded for other reasons as appropriate for the latter type of coupling takes J_0 4.5, about the same numerically as the experimental values of the former type of couplings.

The present results are fully consistent with the view that an approximation to the Karplus relationship can be applied to values of $^3J_{C,H}$ in these cyclic systems,[18] allowance being made for the effect of electronegative substituents on the coupling parameters. Some of the values help to define the appropriate curve for systems with several chlorine atoms; and others, which have been assigned by using the assumed curve, help to confirm it. Allowance needs to be made, however, for conformational averaging of coupling constants for compounds existing in more than one conformation [as must be the case for (4)], and for intramolecular distortions in heavily substituted systems.

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