Naphthalene Dichloride and its Derivatives. Part II.[1] 1,2,3-Trichloro-1,2-dihydronaphthalene from the Dehydrochlorination of Naphthalene δ-Tetrachloride; a Comparison of Vicinal Coupling Constants in the ^{1}H Nuclear Magnetic Resonance Spectra of Some 1,2-Dihydronaphthalenes, Tetralins, and Related Compounds

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1,2,3-Trichloro-1,2-dihydronaphthalene has been prepared by the partial dehydrochlorination of naphthalene δ-tetrachloride, and has been characterised spectroscopically and kinetically. Vicinal coupling constants in the ^{1}H n.m.r. spectra of some 1,2-dihydronaphthalenes are compared with related values for other systems.

THE naphthalene dichlorides remain elusive, though they are reported in early literature summarised in Part I,[1] where we described the preparation and properties of a 1,2,3,4,8-pentachloro-1,2-dihydronaphthalene. In our search for less highly chlorinated derivatives, we have now investigated some possible routes from the naphthalene tetrachlorides, and in this paper we describe the properties of a 1,2,3-trichloro-1,2-dihydronaphthalene obtained from naphthalene δ-tetrachloride.

EXPERIMENTAL

Spectra were determined with the following instruments; ^{1}H n.m.r., a Varian A60 or T60; i.r., a Perkin-Elmer 237; u.v., a Unicam SP 800 spectrometer.

The naphthalene tetrachlorides have been described.[2] Naphthalene (71 g) was allowed to react with chlorine (49 g) in carbon tetrachloride (750 ml) containing a trace (*ca.* 0·1 g) of benzoyl peroxide and brightly illuminated by sunlight. The bulk of the ε- and γ-isomers were removed by crystallisation; the residue was chromatographed on silica gel deactivated by the addition of *ca.* 17% of water, hexane and carbon tetrachloride being used as successive eluants. A fraction (*ca.* 6 g) containing mainly naphthalene δ-tetrachloride was obtained, and this was rechromatographed twice, carbon tetrachloride being used as eluant. The final product, free from isomeric impurities as determined by t.l.c. on silica-gel plates, was recrystallised from methanol, and gave naphthalene δ-tetrachloride (3 g), m.p. 95—96 °C.

Kinetics of Alkaline Dehydrochlorination.—The rates of alkaline dehydrochlorination of the naphthalene tetrachlorides have been examined previously and used to help in structural assignments by Schütz and Hahnfeld[3] and by ourselves[4] but no direct measurements have till now been made in the 1,2-dihydronaphthalene series. We used essentially the method described elsewhere.[5]

The initial concentration of base was in the range 0·04—0·05M, and that of the substrate in the range 0·25—0·5mM, thus ensuring good first-order kinetic behaviour for the development of chloride ions. Infinity titrations agreed satisfactorily with calculated values.

Table 1 shows the kinetic behaviour of naphthalene δ-tetrachloride (0·2834mM) with sodium methoxide (0·0478M) in methanol–acetone (4 : 1) at 25·0 °C. The rate coefficients calculated for the two stages of dehydrochlorination from these results are $k_2 = 10·7$ and 0·150 l mol^{-1} min^{-1}.

TABLE 1

t/min	1·10	1·50	2·00	2·50
Titre (ml 0·00102N-AgNO$_3$)	1·23	1·47	1·73	1·96
t/min	3·00	3·83	5·00	7·00
Titre (ml 0·00102N-AgNO$_3$)	2·12	2·38	2·59	2·80
t/min	10·00	20·00	40·00	70·01
Titre (ml 0·00102N-AgNO$_3$)	2·92	3·13	3·54	3·81
t/min	110·00	160·00	220·00	290·05
Titre (ml 0·00102N-AgNO$_3$)	4·23	4·60	4·87	5·10

Isolation and Characterisation of 1,2,3-*Trichloro*-1,2-*dihydronaphthalene.*—This compound, the intermediate in the alkaline dehydrochlorination of naphthalene δ-tetrachloride, proved very difficult to purify completely, since it could not be crystallised from a solvent, and decomposed very easily when submitted to chromatography. In a typical experiment, naphthalene δ-tetrachloride (0·12 g) was dissolved in methanol (23 ml) and acetone (6 ml). To this mixture was added sodium methoxide (2·9 ml, 0·19M) at 25 °C. After 75 min the mixture was added to diethyl

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[1] Part I, P. B. D. de la Mare and H. Suzuki, *J. Chem. Soc.* (*C*), 1968, 1159.

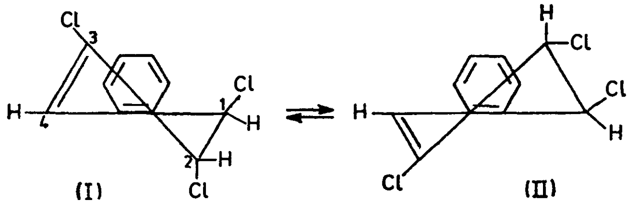
[2] P. B. D. de la Mare, M. D. Johnson, J. S. Lomas, and V. Sanchez del Olmo, *J. Chem. Soc.* (*B*), 1966, 827.

[3] F. Schütz and K. Hahnfeld, *Chem. Ber.*, 1952, **85**, 131.

[4] P. B. D. de la Mare, R. Koenigsberger, and J. S. Lomas, *J. Chem. Soc.* (*B*), 1966, 834.

[5] G. W. Burton and P. B. D. de la Mare, *J. Chem. Soc.* (*B*), 1970, 897.

ether (150 ml). The resulting solution was washed several times with water, dried (Na_2SO_4), and filtered. Removal of the solvent under reduced pressure then gave a liquid, the ^1H n.m.r. spectrum of which characterised the formation of the 1,2,3-dichloro-1,2-dihydronaphthalene (I).

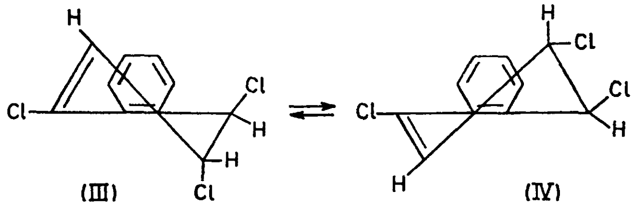


The gross features of the spectrum in deuteriochloroform, with tetramethylsilane as internal reference, showed the presence of aromatic protons (multiplet, τ 3·0—2·4); an olefinic proton (4-H, singlet, τ 3·2); and two alicyclic protons (2- and 1-H, doublets, τ 5·2 and 4·8, $J_{1.2}$ 2·3 Hz). Expansion showed splitting of the signal at τ 5·2 (*J* 0·7—0·8 Hz); that for 4-H was broadened and partially resolved into a doublet, *J ca.* 0·5 Hz. The spectrum was essentially unchanged in CCl_4; in benzene, the signals for all the non-aromatic protons were shifted upfield by *ca.* τ0·4.

This crude product still contained a little naphthalene δ-tetrachloride, as well as the product of full dehydrochlorination. T.l.c. on silica gel with n-hexane, gave a product which was extracted with acetone. Removal of the acetone left as a residue a liquid which crystallised at *ca.* −5 °C. It still contained a trace of the final product of dehydrochlorination as impurity; $\lambda_{max.}$ (cyclohexane) 231 (ε 20,000) and 283 (5900) nm, $\lambda_{infl.}$ 297 (ε 4600), 303 (3600), and 314 (2500) nm, $\nu_{max.}$ (CS_2 or CCl_4) 675s, 730m, 755m, 763m, 792m, 838w, 860w, 888m, 920w, 942w, 990m, 1072m, 1120m, 1125m, 1185m, 1195s, 1220w, 1250w, 1270w, 1330w, 1365m, 1440w, 1450w, 1460w, 1470w, 1489w, 1560w, 1574w, 1608w, and 1636m cm^{-1}.

Kinetics of Dehydrochlorination of Derivatives of 1,2-*Dihydronaphthalene*.—The kinetics of dehydrochlorination of 1,2,3-trichloro-1,2-dihydronaphthalene were determined independently, to characterise it and to obtain a separate estimate of the rate coefficient for the second stage of dehydrochlorination of naphthalene δ-tetrachloride. The resulting rate coefficient, $k_2 = 0{\cdot}148$ l mol^{-1} min^{-1}, for the organic chloride (0·4934mM) with sodium methoxide (0·0479M) in methanol–acetone (4 : 1) at 25 °C, agreed well with that determined from the kinetics of dehydrochlorination of naphthalene δ-tetrachloride treated as two consecutive first-order reactions ($k_2 = 0{\cdot}150$ l mol^{-1} min^{-1}).

Samples of the product of partial dehydrochlorination of naphthalene δ-tetrachloride isolated after only about half of the total amount of chloride ion had been liberated showed in the ^1H n.m.r. spectrum not only the signals derived from the protons of the starting material and of the main intermediate [(I) $\rightleftharpoons$ (II)], but also a doublet (*J* 6 Hz, slightly split further, apparently by long-range coupling) at τ 3·7 ($CDCl_3$). This we regard as a signal from the 3-proton of 1,2,4-trichloro-1,2-dihydronaphthalene [(III) $\rightleftharpoons$ (IV)]; the signals from the 1- and 2-protons would be expected to be obscured by the complex absorption pattern of the unchanged δ-tetrachloride. The proportion of this intermediate was estimated to be 15—17% of the total intermediate present. Partial dehydrochlorination of naphthalene γ-tetrachloride gave a product having absorption in the same region, and also a quartet [two doublets, τ 5·1 and 5·2, signals from the 2-proton of (III); $J_{2.3}$ *ca.* 7 Hz, $J_{1.2}$ *ca.* 2 Hz].



Better ^1H n.m.r. spectra of these intermediates were obtained by adding a small amount of methanolic *ca.* 5M-sodium methoxide to a solution of the appropriate tetrachloride in CCl_4 or in deuteriochloroform contained within an n.m.r. tube. A little D_2O was then added, the tube was shaken, and the ^1H n.m.r. spectrum was recorded. The following spectra data for 1,2,4-trichloro-1,2-dihydronaphthalene derived from naphthalene δ-tetrachloride in CCl_4 were obtained: τ 5·13 (q, 2-H), 4·82 (1-H), and 3·71 (q, 3-H) ($J_{1.2}$ 2·2—2·3 Hz, $J_{2.3}$ 6·4—6·7 Hz, $J_{1.3}$ 1·3 Hz). It was not possible to observe the resonance of 1-H free from signals of other components of the mixtures, nor was it possible to characterise the aromatic signals. The multiplicity of 1-H has therefore not been directly determined, but it should be a quartet with *J* 2·2 and 1·3 Hz. Under these conditions of reaction, the proportion of 1,2,4-trichloro-1,2-dihydronaphthalene formed from naphthalene δ-tetrachloride was *ca.* 24% of the total intermediate present after 20% reaction, and 24 ± 2% after 57% reaction.

Related Systems.—Elsewhere [6] we have described the ^1H n.m.r. spectrum of *trans*-9-acetoxy-10-chloro-9,10-dihydrophenanthrene. The coupling constant $J_{9.10}$ for the corresponding *cis*-isomer has now been determined from the spectrum of a mixture of the two isomers obtained by addition of chlorine acetate (ClOAc) to phenanthrene, as described in a preliminary communication.[7] The corresponding coupling constants, $J_{1.2}$, for the adducts from acenaphthylene, namely *cis*- and *trans*-1-acetoxy-2-chloroacenaphthene, have also been identified.[7] The values are in Table 2.

DISCUSSION

Intermediates in the Dehydrochlorination of Naphthalene δ-*Tetrachloride*.—We deduced [4] that partial alkaline dehydrochlorination of naphthalene δ-tetrachloride gave an intermediate of structure (I). In confirmation, the u.v. spectrum shows a double bond conjugated with a benzene ring (absorption at 283 nm). Of its three non-aromatic protons, one is split in the n.m.r. spectrum only by long-range coupling, and hence must be in the 4-position. The smallness of the value of the coupling constant, $J_{1.2}$ 2·3 Hz, for the remaining hydrogen atoms shows that the intermediate exists largely in conformation (I), with the large chlorine substituents both pseudo-axial, rather than as the conformational isomer

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[6] P. B. D. de la Mare, A. Singh, E. A. Johnson, R. Koenigsberger, J. S. Lomas, V. Sanchez del Olmo, and Anne M. Sexton, *J. Chem. Soc.* (*B*), 1969, 717.

[7] P. B. D. de la Mare, Charmian J. O'Connor, M. J. Rosser, and M. A. Wilson, *Chem. Comm.*, 1970, 731.

(II). It is probable that the preference for the former arises because in (I) steric interactions are minimised not only between adjacent chlorine atoms [in (II) *ca.* 3·3 and 3·0 Å apart; *cf.* Cl–Cl non-bonding internuclear touching distance, 3·6 Å] but also between the 1-Cl and the 8-proton [in (I) 3·5 Å; in (II) 2·4 Å; *cf.* Cl–H non-bonding touching distance, 3·0 Å], whilst there is no large repulsion between other non-vicinal substituents. Some other 1,2-dihydronaphthalenes[8-11] are known to have pseudo-axial dispositions of large 1-substituents. In contrast, a single bulky 2-substituent can prefer the equatorial position.[12]

One of the minor products of the dehydrochlorination of naphthalene δ-tetrachloride is 1,4-dichloronaphthalene,[4] which cannot be derived from (I), and hence must come *via* the alternative structurally isomeric intermediate (III) $\rightleftharpoons$ (IV), which is also the presumed intermediate in the dehydrochlorination of naphthalene γ-tetrachloride. We have now found that the ^{1}H n.m.r. spectra of the crude products of partial dehydrochlorination of each of these tetrachlorides show evidence for the presence, in small proportion, of a compound having the signal of a vinylic hydrogen atom split by coupling with a vicinal hydrogen atom, the coupling constant being in the expected range, and presumed therefore to be this intermediate. Though more unstable to isolation than (I), it must be slowly dehydrochlorinated, and so must have the *trans*-configuration shown in (III) $\rightleftharpoons$ (IV); the smallness of the alicylic coupling constant in the ^{1}H n.m.r. spectrum shows that (III) predominates. It must, therefore, be produced from naphthalene δ-tetrachloride by relatively rapid elimination of (1-H, 2-Cl), presumably through the conformation with these atoms respectively pseudo-axial and axial, as we deduced earlier.[4]

Positions of Conformational Equilibrium as determined from Vicinal Coupling Constants in 1,2-*Dihydronaphthalenes and Tetralins.*—Vicinal 1,2-coupling constants are now commonly used, as we have done for the 1,2-dihydronaphthalenes, to help the assignment of structure. Developing from this have come attempts to make quantitative estimates of the positions of equilibrium in suitable cases in which more than one conformational isomer may be present.[13-15] The basis of any such application is the use of the Karplus relationship[16] relating the coupling constant (J^{ϕ}) to the dihedral angle (ϕ) between the vicinal CH bonds [equations (1a) and (1b)] together with equation (2) which is written for a situation when two conformations A and B (expected coupling constants J_A and J_B) are in mobile equilibrium with proportions α and (1 − α) respectively. Such a treatment has been applied to the unsubstituted 1,2-dihydronaphthalene system and to some of its derivatives by Katritzky, Cook, and their co-workers.[8,17]

$$J = J^0 \cos^2 \phi - 0{\cdot}3 \; (0 \leqslant \phi \leqslant 90°) \qquad (1a)$$

$$= J^{180} \cos^2 \phi - 0{\cdot}3 \; (90 \leqslant \phi \leqslant 180°) \qquad (1b)$$

$$J_{\text{obs}} = \alpha J_A + (1 - \alpha) J_B \qquad (2)$$

During this and related[18] work we have recorded the ^{1}H n.m.r. spectra of some 1,2-dihydronaphthalenes. The structures of two or these [(I) $\rightleftharpoons$ (II) and (III) $\rightleftharpoons$ (IV)] have already been noted. The ^{1}H n.m.r. spectrum defines that a third has the structure (V) $\rightleftharpoons$ (VI) (R^1 = H or Me; R^2 = Me or H). The

TABLE 2

Coupling constants, and approximate dihedral angles, for some derivatives of 1,2-dihydronaphthalene, acenaphthene, and 9,10-dihydrophenanthrene

Compound	Observed coupling (Hz)	Possible conformers: hydrogen positions (dihedral angles)	Conformer with a'a' protons (% calc.)
trans-1,2,3-Trichloro-1,2-dihydronaphthalene (I) $\rightleftharpoons$ (II)	$J_{1,2}$ 2·3	a'a' $\rightleftharpoons$ e'e' (170° $\rightleftharpoons$ 70°)	17
trans-1-Chloro-3,4-dihydro-4-(or 3-)hydroxy-3-(or 4-)methoxy-2-methylnaphthalene (V) $\rightleftharpoons$ (VI)	$J_{3,4}$ 7·8	a'a' $\rightleftharpoons$ e'e' (170° $\rightleftharpoons$ 70°)	71
trans-1,2,4-Trichloro-1,2-dihydronaphthalene (III) $\rightleftharpoons$ (IV)	$J_{1,2}$ 2·2	a'a' $\rightleftharpoons$ e'e' (170° $\rightleftharpoons$ 70°)	16
trans-1-Acetoxy-2-chloroacenaphthene[6]	$J_{1,2}$ 1·5	One conformation only (*ca.* 120°)	
cis-1-Acetoxy-2-chloroacenaphthene	$J_{1,2}$ 6·5	One conformation only (0°)	
trans-9-Acetoxy-10-chloro-9,10-dihydrophenanthrene	$J_{9,10}$ 3·2	a'a' $\rightleftharpoons$ e'e' (170° $\rightleftharpoons$ 70°)	26
cis-9-Acetoxy-10-chloro-9,10-dihydrophenanthrene	$J_{9,10}$ 4·0	a'e' $\rightleftharpoons$ e'a' (50° $\rightleftharpoons$ 50°)	

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[8] M. J. Cook, A. R. Katritzky, F. C. Pennington, and B. M. Semple, *J. Chem. Soc.* (*B*), 1969, 523.

[9] D. Cohen, I. T. Millar, H. Heaney, P. R. Constantine, A. R. Katritzky, B. M. Semple, and M. J. Sewell, *J. Chem. Soc.* (*B*), 1967, 1248.

[10] D. C. Ayres and J. A. Harris, *Chem. Comm.*, 1969, 1135.

[11] M. K. Seikel, F. D. Hostettler, and D. B. Johnson, *Tetrahedron*, 1968. **24**, 1475; F. D. Hostettler and M. K. Seikel, *ibid.*, 1969, **25**, 2325.

[12] H. Lehmkuhl, *Chimia*, 1970, **24**, 182.

[13] R. J. Ferrier and G. H. Sankey, *J. Chem. Soc.* (*C*), 1966, 2345.

[14] R. J. Abraham, H. Gottschalk, H. Paulsen, and W. A. Thomas, *J. Chem. Soc.* (*C*), 1965, 6268.

[15] S. Sternhell, *Rev. Pure Appl. Chem.*, 1964, **14**, 15; *Quart. Rev.*, 1969, **23**, 236.

[16] M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11; *J. Amer. Chem. Soc.*, 1963, **85**, 2870.

[17] M. J. Cook, *Tetrahedron Letters*, 1969, 2893.

[18] G. Cum, P. B. D. de la Mare, M. D. Johnson, and J. S. Lomas, *J. Chem. Soc.* (*B*), 1967, 244.

results are recorded in Table 2, together with some values for related derivatives of acenaphthene and of 9,10-dihydrophenanthrene.[6] More extensive results have been obtained in the tetralin series,[1,2,5,18,19] and some of these are recorded in Tables 3 and 4. In trying to obtain estimates of the positions of conformational equilibrium in our systems, which are heavily substituted with electron-withdrawing groups, values of J^{180} and J^{0} need first to be chosen. Values for unsubstituted systems (*cf.* ref. 8) are not applicable, since the electronegativities of attached groups have a well recognised effect on vicinal coupling constants. We have chosen J^{180} = 12·4 Hz to agree with the highest values which we have recorded among the substituted tetralins, a value which seems very well in line with accepted trends. The value of J^{0} is a little more difficult to assign; J^{0} = 6·8 Hz would give agreement with the experimental value (Table 2) for the eclipsed protons in *cis*-1-acetoxy-2-chloroacenaphthene, but in comparison with the less rigid 1,2-dihydronaphthalene and tetralin systems this molecule is expected to be strained in a direction which would reduce the observed coupling

TABLE 3

Alicyclic vicinal coupling constants for some halogen-substituted tetralins derived from naphthalene [2]

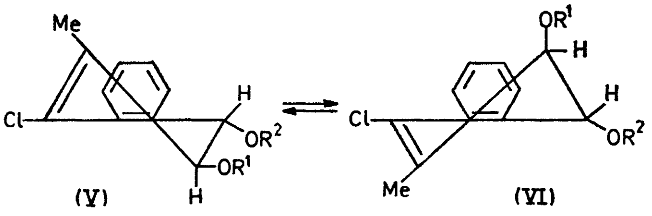
Compound	Observed coupling (Hz)	Possible conformers: hydrogen positions (dihedral angles)	Conformer a′a or aa (% calc.)
Naphthalene α-tetrachloride [a]	$J_{2.3}$ 10·8	aa $\rightleftharpoons$ ee (187° $\rightleftharpoons$ 67°)	90
Naphthalene γ-tetrachloride [a]	$J_{1.2}$ 8·1	a′a $\rightleftharpoons$ e′e (170° $\rightleftharpoons$ 70°)	74
	$J_{2.3}$ 8·0	aa $\rightleftharpoons$ ee (187° $\rightleftharpoons$ 67°)	65
Naphthalene δ-tetrachloride	$J_{1.2}$ 7·6	a′a $\rightleftharpoons$ e′e (170° $\rightleftharpoons$ 70°)	69
	$J_{2.3}$ 10·9	aa $\rightleftharpoons$ ee 187° $\rightleftharpoons$ 67°	91
Naphthalene acetoxytrichloride	$J_{1.2}$ 7·0	a′a $\rightleftharpoons$ e′e (170° $\rightleftharpoons$ 70°)	63
	$J_{2.3}$ 11·0	aa $\rightleftharpoons$ ee 187° $\rightleftharpoons$ 67°	92
Naphthalene hydroxytrichloride	$J_{1,2}$ 8·3	a′a $\rightleftharpoons$ e′e (170° $\rightleftharpoons$ 70°)	76
	$J_{2.3}$ 10·6	aa $\rightleftharpoons$ ee 187° $\rightleftharpoons$ 67°	88

[a] Coupling constants for these compounds are revised values determined in the course of this work.

TABLE 4

Alicyclic vicinal coupling constants for some halogenotetralins derived from substituted naphthalenes [1,2,5,13,15]

Compound	Observed coupling (Hz)	Possible conformers: hydrogen positions (dihedral angles)	Conformer a′a or aa (% calc.)
2-Methylnaphthalene tetrachloride	$J_{3.4}$ 8·4	a′a $\rightleftharpoons$ e′e (170° $\rightleftharpoons$ 70°)	77
2-Methylnaphthalene acetoxytrichloride	$J_{3.4}$ 8·6	a′a $\rightleftharpoons$ e′e (170° $\rightleftharpoons$ 70°)	79
1-Chloronaphthalene tetrachloride	$J_{2.3}$ 12·0	aa $\rightleftharpoons$ ee (187° $\rightleftharpoons$ 67°)	100
1-Bromonaphthalene tetrachloride	$J_{2.3}$ 11·4	aa $\rightleftharpoons$ ee (187° $\rightleftharpoons$ 67°)	96
1,2,3,4,5-Pentachloro-1,2,3,4-tetrahydro-6-methylnaphthalene	$J_{2.3}$ 8·0	aa $\rightleftharpoons$ ee (187° $\rightleftharpoons$ 67°)	65
1-Methylnaphthalene tetrachloride	$J_{2.3}$ 12·0	aa $\rightleftharpoons$ ee (187° $\rightleftharpoons$ 67°)	100
1-(Chloromethyl)naphthalene tetrachloride	$J_{2.3}$ 11·6	aa $\rightleftharpoons$ ee (187° $\rightleftharpoons$ 67°)	98
1-Isopropylnaphthalene tetrachloride	$J_{2.3}$ 11·2	aa $\rightleftharpoons$ ee (187° $\rightleftharpoons$ 67°)	94
1,2,3,4,4-Pentachloro-1-methyltetralin	$J_{2.3}$ 11·5	aa $\rightleftharpoons$ ee (187° $\rightleftharpoons$ 67°)	97
1,2,3-Trichloro-4-hydroxy-4-methyltetralin	$J_{2.3}$ 11·6	aa $\rightleftharpoons$ ee (187° $\rightleftharpoons$ 67°)	98
1,1,2,3,4-Pentachloro-2-methyltetralin	$J_{1,2}$ 5·8	a′a $\rightleftharpoons$ e′e (170° $\rightleftharpoons$ 70°)	51



(V) (VI)

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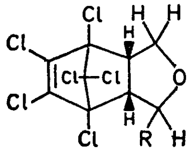
[19] P. B. D. de la Mare and H. Suzuki, *J. Chem. Soc.* (*C*), 1967, 1586; G. Cum, P. B. D. de la Mare, and M. D. Johnson, *J. Chem. Soc.* (*C*), 1967, 1590.

constant.[16,20] We have assumed, therefore, that a somewhat larger value, J^{0} 8·3 Hz, is more appropriate. This gives agreement with the value J^{0} 8·0 Hz for the eclipsed protons in derivatives of 4,5,6,7,8,8-hexachloro-1,3,3a,4,7,7a-hexahydro-4,7-methanoisobenzofuran (VII; R = Cl, OH, OAc).[21] Values in the range 8—9 Hz have also been reported for the camphane-2,3-diols.[22] The calculations of isomeric proportions are not, in fact, very much altered by a change in the assumed value of J^{0} over a range of ±1 Hz.



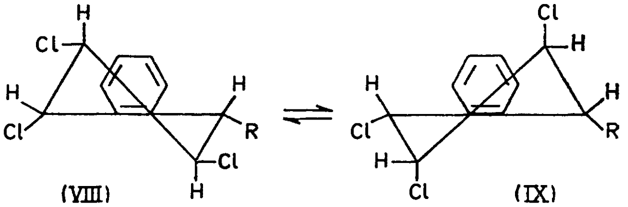
(VII)

To use equations (1a), (1b), and (2) for comparison with experiment, we need to adopt reasonable geometrical models for our systems. We have assumed normal bond lengths, with conventional tetrahedral and trigonal angles, and have neglected non-bonding interactions. We have assumed also that the tetralins exist in the half-chair conformation, rather than the boat or any distorted form; and that the 1,2-dihydronaphthalenes also exist in the related conformation. Such assumptions are consistent with physical evidence [23] and theoretical calculations [24] on related systems. The estimated values of ϕ are given in the Tables.

Our results for compounds in which the conformational equilibrium does not change the dihedral angle appreciably (*i.e.*, those involving e'a' $\rightleftharpoons$ a'e' or a'e $\rightleftharpoons$ e'a equilibria) include 13 from the tetralin series.* The mean value for these compounds (J 3·1 Hz) agrees well with the theoretical curve, the range of values being 2·4—3·8 Hz. We can calculate also the expected value of the $J_{1,2}$ coupling constant in naphthalene ε-tetrachloride, in which the conformations are energetically equivalent and the expected coupling constant is therefore $0{\cdot}5(J^{170} + J^{70}) = 6{\cdot}1$ Hz (Found: 6·4 Hz, a revision of the value reported previously).

Our experimental results therefore agree quite well with the assumed relations of equations (1a), (1b), and (2). The deviations (±0·7 Hz) no doubt represent minor structural influences either on the geometry of the system or on the coupling constants. Among such influences are included the geometrical relationships of the electronegative substituents to the coupling path [25] including the influence of relatively distant electronegative groups,[26] and intramolecular non-bonding interactions, which we shall consider later. Probably an uncertainty of up to ±1 Hz should be allowed for such factors, and hence the calculations of positions of equilibrium based on our values and given in the Tables should be considered as subject to an uncertainty of up to ±10 units %. The following qualitative conclusions can be drawn with some confidence. (i) The two *trans*-trichloro-1,2-dihydronaphthalenes (Table 2) exist mainly but not exclusively with protons e'e' and hence chlorines a'a'; (ii) *trans*-1-chloro-3,4-dihydro-4-(or 3-)hydroxy-3-(or 4-)methoxy-2-methylnaphthalene (Table 2) in solution is predominantly in the form (V) with protons a'a'. Analogously, a closely balanced conformational situation, which can be altered by change in solvent, has been reported for 2,3-dihydro-2,3-dihydroxybenzoic acid.[27] (iii) The four naphthalene tetrachlorides (Table 2) all (with the possible exception of the α-isomer) exist in solution as mixtures of conformers. It will be remembered that their products of dehydrochlorination also indicate in every case the accessibility of both conformers. (iv) The same is true of the derivatives of 2-methylnaphthalene, but the derivatives of 1-methyl-, 1-chloro-, and 1-bromo-naphthalene exist with a greater preponderance of the isomer with two axial 2,3-hydrogen atoms (Table 4).

For some of the adducts from naphthalene (Table 3) the coupling constants give two estimates of the position of conformational equilibrium. In each case the estimates agree as to the predominant conformer, and the numerical agreement is fair for naphthalene γ-tetrachloride. Discrepancies exist, however, for naphthalene δ-tetrachloride and its conformational analogues, naphthalene acetoxy- and hydroxy-trichoride. All these compounds have the rather asymmetrical structure represented by the equilibrium (VIII) $\rightleftharpoons$ (IX). In either of these conformations, intramolecular non-bonding interactions are rather unsymmetrical; and we believe that they result in significant distortions of the molecules so that the discrepancies revealed by the coupling constants probably do not represent a real deviation from the Karplus relationship, but instead a departure from the idealised dihedral angles on which our models are based. Distortions of this kind may be more generally important and we expect to return to this matter in further papers.



(VIII) (IX)
(R=Cl,OH,OAc)

The Acenaphthene and 9,10-Dihydrophenanthrene

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* Details are given in the cited papers.

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Systems.—Our values for the coupling constants in the 1-acetoxy-2-chloroacenaphthenes (Table 2) are in good agreement with literature values[15] for 1-chloro- and 1-acetoxy-acenaphthenes (*viz*., J^0 7·4, 7·2 Hz, J^{120} 2·4, 2·5 Hz), the expected influence of electronegativity being taken into account. All the values lie somewhat below the relation which we have taken to represent the situation for the tetrahydronaphthalene derivatives. Strain in the system accounts for this in the case of the value of J^0 (Table 2; 6·5 Hz) as we have noted. In the case of the smaller coupling (Table 2; 1·5 Hz), however, it is possible that the idealised dihedral angle of 120° is not correct. No accurate *X*-ray diffraction measurement is available as far as we are aware, but a value *ca*. 112° is by no means inconsistent with an estimate (112° ± 23°) derived from Erlich's results.[28]

As far as the 9,10-dihydrophenanthrene system is concerned, our values in Table 2 are in satisfactory agreement with literature values for 9-dimethylamino-9,10-dihydro-4,5-dimethylphenanthrene[29] when the electronegativity correction is taken into account. Application of equations (1a), (1b), and (2) to estimate the position of conformational equilibrium for *trans*-9-acetoxy-10-chloro-9,10-dihydrophenanthrene results in the reasonable conclusion (Table 2) that this compound exists mainly but not exclusively as the conformer with protons e'e' and hence with the substituents a'a'.

Long-range Couplings.—The values of the long-range couplings observed in ^{1}H n.m.r. spectra of the two isomeric trichloro-1,2-dihydronaphthalenes are in each case consistent with what would be expected for the predominant conformation. The splitting, *J* 0·8 Hz, observed in the signal for the alicyclic proton at τ 5·2 in (I) $\rightleftharpoons$ (II) is assigned as an allylic coupling of the equatorial 2-H with the vinylic 4-H. Such couplings have been observed to range from +1·6 to —3·5 Hz for cyclic compounds, depending on the dihedral angle between the allylic hydrogen atom and the double bond.[30] From a model, this angle is *ca*. 155°, whence a value between 0 and 1 Hz would be expected; values of 0·5 and 0·95 Hz have been recorded[30] for two examples in which the dihedral angle is estimated to be 160°. The broadening of the signal for the 4-H results in its incomplete resolution into a doublet, and probably arises from long-range coupling with the aromatic protons.

The splitting (1·3 Hz) of the vinylic proton at τ 3·7 in (III) $\rightleftharpoons$ (IV) is considered to be a propane-like coupling between the 1-H and 3-H, which have a *trans*- or W-like relationship for which propanic couplings lie between 1 and 2 Hz.[30] The signal for 1-H is, however, obscured by signals from other components of the reaction mixture, thus preventing confirmation of this assignment.

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