Rotational Isomerism. Part XVIII.[1] Rotamer Populations in Solution of Some Polychlorinated Butanes: a Molecular Mechanics and Nuclear Magnetic Resonance Study

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The ^1H n.m.r. spectra of *meso* (1) and racemic (2) 1,1,2,3,4,4-hexachloro- and *meso* (3) and racemic (4) 1,2,3,4-tetrachloro-butanes are reported and analysed in polar and non-polar solvents. Molecular mechanics calculations and classical solvent theory were used to provide information on the rotamer energies in these molecules and these, together with the observed proton couplings (and in one case dipole moment), allowed a determination of the rotamer populations. Compound (1) exists primarily in one conformation, (2) and (4) as two populated rotamers, but (3) appears to have at least four populated rotamers. The observed rotamer populations and energies are in general in good agreement with the calculated values, and this suggests that this technique could be of value in determining rotamer populations in complex molecules.

THE determination of rotamer populations in substituted ethanes from the observed proton couplings has been a widely used technique in recent years (*cf.* ref. 1 and other papers in this series). However the use of this technique to study the more complex problems of rotational isomerism in propanes and butanes has been much less investigated mainly because of the complexity of both the spin systems and the rotamer populations in the general case. (A substituted butane of no symmetry has 27 different rotamers and could be a general 10-spin system.) Thus most studies have been concerned with more symmetric molecules such as 1,2-dihalogeno-propanes,[2,3] 2,3-dihalogeno-butanes,[4,5] and 2,2-dimethylbutanes [6] which are simply methyl and t-butyl substituted ethanes. However, Sheppard and his co-workers have performed a detailed i.r. and n.m.r. investigation of chlorinated propanes [7,8] and have stressed the importance of the parallel 1,3-interactions in determining conformer populations, and 1,2,3-tribromopropane was also shown to exist predominantly in one conformation.[9] A similar investigation on

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[6] G. M. Whitesides, J. P. Sevenair, and R. W. Goetz, *J. Amer. Chem. Soc.*, 1967, **89**, 1135.

[7] A. B. Dempster, K. Price, and N. Sheppard, *Spectrochimica Acta*, 1969, **25A**, 1381.

[8] A. B. Dempster, K. Price, and N. Sheppard, *Spectrochimica Acta*, 1971, **27A**, 1563, 1579.

[9] L. Ernst and T. Schaefer, *Canad. J. Chem.*, 1973, **51**, 565.

2,4-disubstituted pentanes[10] also revealed one predominant conformation in certain cases, but there has been no systematic investigation of halogenobutanes.

meso (1) and racemic (2) 1,1,2,3,4,4-hexachloro- and *meso* (3) and racemic (4) 1,2,3,4-tetrachloro-butanes provide a reasonable set of compounds for a detailed investigation, and we shall show that the combination of n.m.r., dipole moment, and molecular mechanics calculations provides a powerful technique for studying rotational isomerism in these systems. During this investigation the ^1H n.m.r. spectrum of (1) was reported briefly and analysed.[11] We shall confirm these authors' conclusions.

EXPERIMENTAL

Samples of compounds (1)—(4) were donated by I.C.I. (MOND and Pharmaceuticals). Subsequently compound (2) was purchased from Aldrich Chemical Co. The n.m.r. spectra were obtained with a Varian HA-100 spectrometer, probe temperature 27°, as 15% (v/v) solutions with tetramethylsilane as internal reference. All the solutions were degassed by the freeze–pump–thaw method, and the average of three spectra (measured by the side-band method) obtained. The final values of the coupling constants and chemical shifts have been obtained using the iterative programs LAOCN3[12] and LACX[13] and the probable and r.m.s. errors are obtained from these programs.

The dipole moment of (4) in n-heptane and benzene solutions was obtained with the apparatus described in ref. 14, but using the Halverstadt–Kumler equation.[15] Extrapolation to infinite dilution gave P_{20} values of 67·62 (n-pentane) and 82·39 cm³ (benzene) which gave dipole moments of 1·18 (pentane) and 1·46 D (benzene) using d^{20} 1·45 and N_D^{20} 1·50.

Spectral Analysis.—The proton resonance spectra of the hexachlorobutanes (1) and (2) are examples of the well-known AA′BB′ spin system.[16] However, because of the very small $^5J_{HH}$ coupling, the spectrum of (1) consists of a simple first-order triplet for each half and that of (2) of six resolved lines (Figure 1) instead of the usual 12 transitions. The analysis of (1) was initially performed from the ^{13}C satellite spectrum, which is first order and these values were consistent with the full spectrum. At this stage our attention was drawn to the results of ref. 11. As our results are identical we shall use these henceforth. The analysis of the more resolved spectrum of (2) was straightforward and is shown in Figure 1 and Table 1.

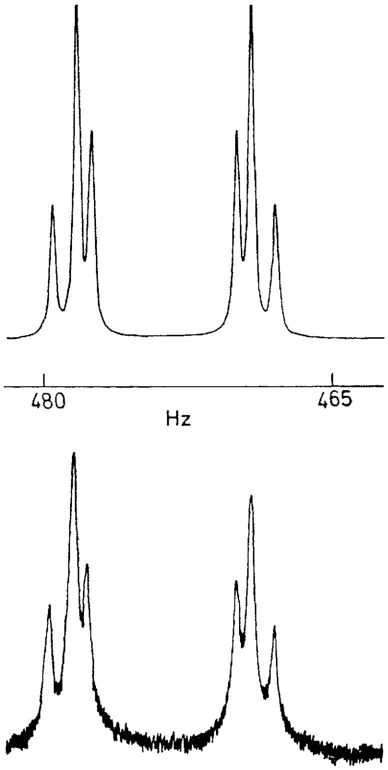

FIGURE 1 Observed (lower) and calculated (upper) 100 MHz ^1H spectrum of the high-field region of racemic $CHCl_2{\cdot}CHCl{\cdot}CHCl{\cdot}CHCl_2$ (2) in n-pentane solution. Frequencies in Hz from Me_4Si

TABLE 1

Proton chemical shifts (δ) and coupling constants (Hz)[a] in *meso* and racemic tetra- and hexa-chlorobutanes

Compound	Solvent	Chemical shifts			$^2J_{HH}$	$^3J_{HH}$			$^4J_{HH}$	
		H(1), H(4)		H(2), H(3)		$J_{12(34)}$		J_{23}	$J_{23(24)}$	
(1)[b]	$CDCl_3$	6·43		4·32		1·71		10·13	−0·1	
(2)	n-Pentane	5·721		4·738		9·20		1·98	−0·15	
	CCl_4	5·763		4·759		9·17		1·99	−0·15	
	CH_2CN	6·030		4·915		8·51		2·31	−0·14	
		1a, 4a	1b, 4b		1a, 1b	1a, 2	1b, 2		1a, 3	1b, 3
(3)	CCl_4	4·107	3·944	4·418	−12·31	3·98	3·68	8·56	−0·18	−0·38
	CH_3CN	2·179[c]	2·078[c]	2·582[c]	−12·56	4·44	3·17	8·76	−0·16	−0·42
(4)	n-Pentane	3·820	3·730	4·563	−10·90	10·48	4·81	1·81	−0·23	−0·28
	C_6D_6	3·447	3·289	4·148	−11·09	9·67	5·14	2·00	−0·17	−0·21
	CH_2Cl_2	3·862		4·615		7·51		1·58	−0·30	

[a] The only $^5J_{HH}$ coupling which is significant (*i.e.* >0·05 Hz) is $J_{1b,4b}$ in (3); 0·46 Hz. [b] $J[^{13}C–H(1)]$ 177·9; $J[^{13}C–H(2)]$ 158·8 Hz. [c] From CH_3CN.

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[10] P. E. McMahon and W. C. Tincher, *J. Mol. Spectroscopy*, 1965, **15**, 180.

[11] J. B. Rowbotham, H. M. Hutton, and T. Schaefer, *Canad. J. Chem.*, 1971, **49**, 806.

[12] S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, 1964, **41**, 3863.

[13] C. Haigh, personal communication.

[14] D. Brennan and C. F. H. Tipper, 'A Laboratory Manual of Experiments in Physical Chemistry,' McGraw-Hill, London, 1967.

[15] J. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.*, 1942, **64**, 2988.

[16] R. J. Abraham, 'Analysis of High Resolution N.M.R. Spectra,' Elsevier, Amsterdam, 1971.

Note that the sign ambiguity characteristic of these spin systems extends only to J_{14} which is zero in both cases. The negative sign of J_{13} follows from the analysis.

Although there have been calculations of a few six-spin systems of the AA′BB′CC′ type, the general properties of this type of spin system have not been discussed in such detail as the properties of the AA′BB′ system. The latter spin system can be considered to be a lower homologue of the AA′BB′CC′ problem. Manatt and Bowers [17] have discussed some of the general features of this spin system. They also presented a set of basic symmetry wave functions and corresponding matrix elements of the Hamiltonian. They concluded that for the general AA′BB′CC′ case it is not possible to derive any explicit expressions for the transition energies and intensities, and furthermore that sub-spectral analysis was of limited value for this spin system.

In accord with this, our procedure was based entirely on iterative computational analysis.

Even so, the complete analysis of the spectra offered some difficulties. While good starting values for the iterative calculation could be obtained for the chemical shifts and geminal and vicinal couplings, this was not the case for the three- and four-bond couplings. For this reason, the values of the three- and four-bond couplings of (1) and (2) (which are not expected to be very sensitive toward the replacement of Cl for H) were successfully extrapolated to the tetrachlorobutanes. Nevertheless, about 15 non-iterative spectra were initially calculated, varying the various parameters, before a reasonable assignment of the observed spectra could be performed. Some particular problems were encountered. In the spectrum of (3) in CCl_4 (Figure 2), although the iteration converged properly, the calculated spectrum did not adequately reproduce the small transitions in the spectrum.

Use was made of the facility of LACX to output the partial derivative of the transitions with respect to the coupling constants and chemical shifts. From this it was observed that these small transitions were affected by the long range coupling constants but that these errors were being swamped by those resulting from the incomplete resolution of the major transitions in the spectrum. This was overcome by iterating on the small lines together with only some of the major peaks, and this gave a better iteration and also a calculated spectrum in complete accord with the observed (Figure 2). An equally good alternative procedure is to increase the weighting factor on the selected transitions, and it would appear that in the case of a complex spectrum containing many unresolved transitions, weighting the single transitions should be routine procedure.

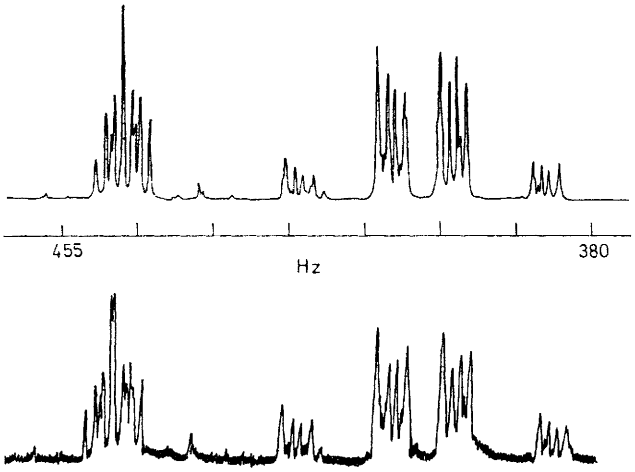

FIGURE 2 Observed (lower) and calculated (upper) 100 MHz ^1H spectrum of *meso*-$CH_2Cl{\cdot}CHCl{\cdot}CHCl{\cdot}CH_2Cl$ (3) in CCl_4 solution. Frequencies in Hz from Me_4Si

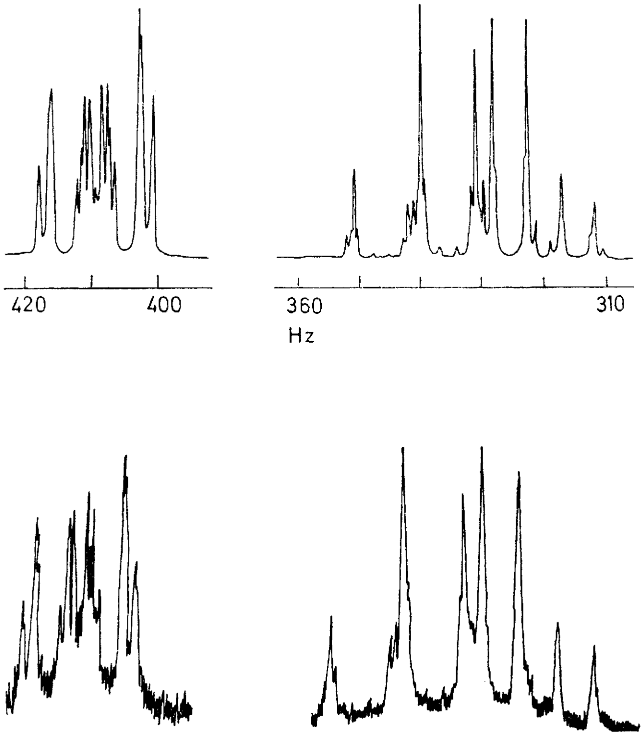

FIGURE 3 Observed (lower) and calculated (upper) 100 MHz ^1H spectrum of racemic $CH_2Cl{\cdot}CHCl{\cdot}CHCl{\cdot}CH_2Cl$ (4) in C_6H_6 solution. Frequencies in Hz from Me_4Si

The spectrum of (4) was rendered difficult by the closely coupled nature of the CH_2 protons. The chemical shift between these protons became so small in CH_2Cl_2 solvent that the spectrum could only be analysed as a deceptively simple $(A_2B)_2$ spectrum from which only the average of any coupling to the CH_2 protons can be determined accurately. In other solvents, this problem was not encountered and the spectrum in C_6H_6 (Figure 3) was analysed normally.

All the results from these analyses are given in Table 1. The errors for (1) which was not an iterative computer analysis are $\pm 0{\cdot}1$ Hz, for (2) the LAOCN3 r.m.s. errors were $\lesssim 0{\cdot}02$ Hz and the probable errors $\lesssim 0{\cdot}006$ Hz for all the solutions studied. For (3) and (4) the increased complexity of the spectra was reflected in the larger values of the r.m.s. errors (*ca.* 0·06 Hz) and probable errors (*ca.* 0·02 Hz).

RESULTS

Rotational Isomerism.—We now use the results in Table 1, together with dipole moment measurements and molecular mechanics and solvation theory calculations, to deduce the rotamer compositions of (1)—(4). The molecular

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[17] S. L. Manatt and M. T. Bowers, *J. Amer. Chem. Soc.*, 1969, **91**, 4381.

mechanics calculations use the program MODELS 2,[18,19] developed from the original MODELS calculations.[20] The standardised geometry used is that of ref. 20. The solvation theory calculations using DIPQUADMOMS have been fully described previously.[21]

As there are a maximum of 27 rotamers for a non-symmetric butane, it is necessary to introduce a systematic nomenclature to define the rotamers. Each rotamer is defined in terms of three dihedral angles W_1 [HC(1)C(2)C(3)], W_2 [C(1)C(2)C(3)C(4)], and W_3 [C(2)C(3)C(4)H] in which the angles are defined as positive for a clockwise rotation from the eclipsed position looking along C(2) ⟶ C(1) (W_1), C(2) ⟶ C(3) (W_2), and C(3) ⟶ C(4) (W_3).

The MODELS 2 calculations use the standardised geometry but iterate on the three dihedral angles W_{1-3}. The minimum energy rotamers and the values of the dihedral angles thus obtained are given in Table 2, together with the calculated solvation energies (from DIPQUADMOMS), using the same minimum energy geometry.

TABLE 2

Calculated rotamer geometries and energies for *meso* and racemic hexachloro- (1) and (2), and tetrachlorobutanes (3) and (4)

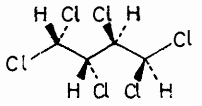
	Geometry			Energy (kcal mol^{-1})	$(E_g - E_s)$[b]		Dipole moment[b]
Rotamer	W_1[a]	W_2[a]	W_3[a]	E_g[a]	$\varepsilon = 1{\cdot}8$	37·5	μ(D)
(1A)	303·2	180·0	57·5	6·8	0·6	1·9	0·2
(1B)	154·6	181·0	57·8	12·0	0·5	2·0	3·2
(2A)	294·5	180·0	294·3	4·9	0·2	0·5	0·1
(2B)	61·6	311·2	62·6	9·6	0·8	2·9	2·8
(3A)	175·9	179·7	181·5	4·3	1·0	2·9	0·0
(3B)	306·7	184·3	182·8	4·6	1·0	3·3	3·3
(3C)	317·0	76·7	306·0	4·6	0·6	2·7	2·7
(3D)	304·4	179·2	52·8	5·2	1·3	3·7	0·0
(3E)	313·3	69·0	41·2	5·2	1·3	3·9	2·5
(4A)	183·2	185·3	302·7	2·7	0·3	0·9	0·0
(4B)	182·6	183·4	43·9	3·6	0·5	2·0	2·7
(4C)	286·0	51·9	45·2	3·9	0·9	3·0	0·8
(4D)	284·3	181·4	43·3	4·6	1·2	4·0	2·3

[a] Output from MODELS 2, iterating on all three dihedrals for minimum energy. [b] Output from DIPQUADMOMS using final MODELS 2 geometries.

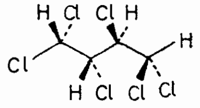
Compound (1).—Our values of the couplings in (1) agree entirely with those of Schaefer *et al.*[11] who obtained for CS_2 and Me_2SO solutions $J_{12(34)}$ 1·80 (1·86), J_{23} 10·14 (10·08), and $J_{13(24)}$ −0·22 (−0·16) Hz. The values of the $^3J_{HH}$ couplings plus the insensitivity of these couplings to the solvent suggests that (1) exists in a single conformation or conformations in which $J_{12(34)}$ is always a *gauche*- and J_{23} always a *trans*-coupling. There are only three distinct conformers satisfying these conditions, (1A—C), and of these (1A) is clearly the most favourable as there are no destabilising parallel 1, 3-Cl · · · Cl interactions, and this was stated by Schaefer *et al.*

The MODELS 2 calculations (Table 2) conclusively confirm these predictions. Conformer (1A) is more stable by *ca.* 5 kcal mol^{-1} than the next rotamer (1B); (1C) is of even higher energy and has not been included. In this case also the solvation energy calculations do not predict any destabilising of (1A) relative to (1B), despite their very different dipole moments (the quadrupole term cancels out the dipole term).

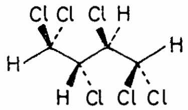
Thus (1A) is the only populated rotamer. This has the immediate consequence of providing values of the rotamer couplings for the CH·CH fragments involved directly from the observed couplings, and these are of value for the remaining compounds.



(1A)

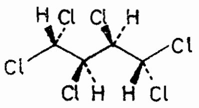


(1B)

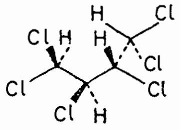


(1C)

Compound (2).—The results of the molecular mechanics and solvation theory calculations for this compound are also given in Table 2. Again in the vapour phase there is only one rotamer (2A), which has significantly no parallel 1,3-Cl · · · Cl interactions. Rotamer (2B) is 4·7 kcal mol^{-1} less stable, which means essentially zero population in this state. In contrast to the *meso*-isomer, the solvation energy of the two rotamers is very different, due to their very different dipole moments, and the energy difference $E_B - E_A$ decreases rapidly on increasing the polarity of the solvent, down to *ca.* 2 kcal mol^{-1} in CH_3CN solution. Thus (2B) will become significantly populated. All other rotamers are >3 kcal mol^{-1} higher in energy than (2A) in all solvents and may be excluded.



(2A)



(2B)

The calculations predict therefore that (2) will exist as a mixture of two rotamers (2A and B), with (2A) predominant, particularly in non-polar solvents. Furthermore as (2A) has *trans*-oriented couplings $J_{12(34)}$ and *gauche*-couplings for J_{23}, whereas (2B) has the reverse, this equilibrium should be observed in the n.m.r. spectrum. The n.m.r. results (Table 1) are in accord with these predictions, J_{12} varying from 9·20 (n-pentane) to 8·51 (CH_3CN) and J_{23} varying from 1·98 (n-pentane) to 2·31 Hz (CH_3CN). The observed couplings can now be analysed in terms of this two rotamer equilibrium, as any observed coupling is simply given by $J^{obs} = n_A J^A + n_B J^B$ where $n_A + n_B = 1$, *i.e.* equation (1) applies.

$$n_A = (J^{obs} - J^B)/(J^A - J^B) \qquad (1)$$

It is merely necessary to obtain the couplings in the distinct rotamers (2A and B). Those in (2B) may be approximated without any serious error to the observed couplings of (1), as they are similarly oriented fragments. The couplings in (2A) may also be derived from those of (1)

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[18] P. Loftus, Ph.D. Thesis, University of Liverpool, 1974.

[19] R. J. Abraham and P. Loftus, *J.C.S. Chem. Comm.*, 1974, 180.

[20] R. J. Abraham and K. Parry, *J. Chem. Soc.* (*B*), 1970, 539.

[21] R. J. Abraham and E. Bretschneider, ' Internal Rotation in Molecules,' ed. W. J. Orville-Thomas, Academic Press, London, 1974, ch. 13.

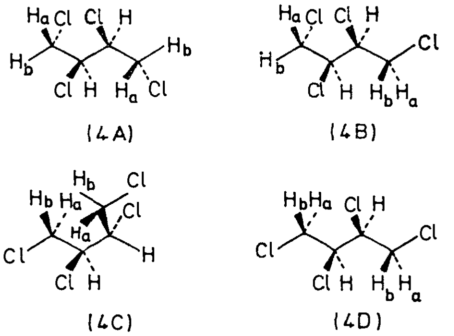
by allowing for the different electronegativities of the fragments involved and using the equations given previously relating vicinal couplings to substituent electronegativity.[22,*] These give calculated values of J^t_{12} and J^g_{23} for (2A) of 9·64 and 1·36 Hz respectively, from the corresponding values in (1) of 10·11 and 1·83 Hz.

As the values of all the couplings for the C(1)C(2) and C(2)C(3) fragments of (2A and B) are now known, the observed couplings when introduced into equation (1) give two independent determinations of n_A and n_B. From the values of J_{12}, we obtain n_A 0·94 (n-pentane) and 0·86 (CH_3CN) and from those of J_{23} values of 0·93 (n-pentane) and 0·89 (CH_3CN), in very close agreement, which is strong support for the above procedure.

The relative rotamer energies obtained from these proportions (note that the statistical weights of both rotamers are one) are $E_B - E_A$ 1·6 in n-pentane and 1·2 kcal mol^{-1} in CH_3CN solution. These will be discussed later.

Compound (4).—It is convenient to consider this compound before the more complex case of the *meso*-isomer (3). The MODELS 2 calculations predict four populated rotamers (Table 2 and Scheme 1) one of which, (4B), has a statistical weight of two. As this compound is less substituted than the hexachlorobutanes (1) and (2) there are many rotamers without parallel 1,3-Cl · · · Cl interactions. Furthermore the three high energy rotamers become relatively more stable in polar solvents and cannot be ignored. At first sight the problem would appear insoluble, as there are more unknowns than equations. However, more detailed inspection combined with the dipole measurements, show that the rotamer populations can be obtained as follows.

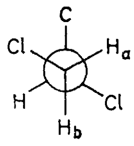
The system may be considered as a general four rotamer case with (4A) predominating, particularly in non-polar solvents. The rotamer couplings for (4A) are $J_{1a,2} = J_t$; $J_{1b,2} = J_g$; and $J_{23} = J_g$. The orientation of J_{23} is the same (J_g) for all the rotamers considered and thus this coupling cannot be used to distinguish between them. This is consistent with the observed value of the coupling of 1·8 (±0·2) Hz which also does not vary in any systematic manner in the solvents studied (Table 1).



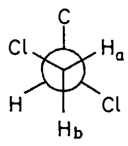
SCHEME 1 Populated rotamers of racemic $CH_2Cl{\cdot}CHCl{\cdot}CHCl{\cdot}CH_2Cl$ (4)

The couplings in the C(1)C(3) fragment in contrast do vary considerably, from 10·48 and 4·81 (n-pentane) to 9·67 and 5·14 in benzene and these may be interpreted as due to the predominant conformer (4A) with increasing proportions of the others. This furthermore assigns the methylene protons, and this assignment is given in Scheme 1.

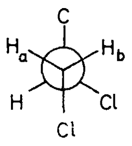
It is now necessary to obtain values of the rotamer couplings in this fragment in order to evaluate the rotamer populations. As previously, our procedure will be to utilise the observed couplings in similarly substituted molecules and then correct for the different substituent electronegativities by means of the equations in ref. 22. It is convenient also to re-draw the rotamer fragments considered in the Newman projections below. Note that rotamer (4B) has two different $CHCl{\cdot}CH_2Cl$ fragments (B_1 and B_2) and the rotamer couplings are the averages of these. Inspection of the Newman projections shows that whilst the assumption of one J_t for the different rotamers is plausible, there will be two distinct values of J_g, one in (4A and B_1) in which the chlorine atoms are *trans*, and the other in ($4B_2$, C, and D) in which the chlorines are *gauche*, which will be termed J_g'. Thus equations (2)—(4), corresponding to (1), for this fragment apply.



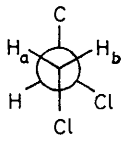
(4A)



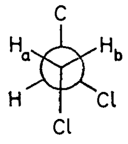
(4B$_1$)



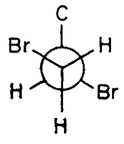
(4B$_2$)



(4C)



(4D)



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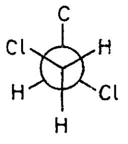
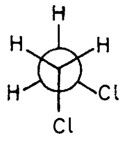


(6)



(7)

$$J_{1a,2} = n_A J_t + n_B(J_t + J_g')/2 + (n_C + n_D)J_g' \tag{2}$$

$$J_{1b,2} = n_A J_g + n_B(J_g + J_t)/2 + (n_C + n_D)J_t \tag{3}$$

$$1 = n_A + n_B + n_C + n_D \tag{4}$$

The observed couplings in 1-(*p*-nitrophenyl)-1,2-dibromoethane (5), which is predominantly in the conformation shown are 11·5 and 4·7 Hz.[23] Correcting for Br $\longrightarrow$ Cl gives J_t 11·1 Hz.

The couplings in 1,2-dichloropropane (6) show a pronounced solvent dependence, varying from 5·90 and 5·15 in DMSO to 9·08 and 4·71 Hz in CCl_4.[2,3] The most stable (but not predominant) conformer is as shown and this would suggest 4·7 Hz as the upper limit for J_g in (4A and B). We take 4·4 Hz.

The *gauche*-coupling in ($4B_2$, C, and D) will be much smaller, due to the orientation of the chlorine atoms and this may be estimated from the analogous coupling in the *gauche*-rotamer of 1,2-dichloroethane (7) of 2·9 Hz,[22] which after correcting for the introduction of the extra carbon atom, becomes 3·2 Hz.

These values of the rotamer couplings can be introduced into equations (2) and (3) together with the observed couplings (Table 1). However, this still leaves three

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[*] These equations were derived only for $CH_2{\cdot}CH_2$ fragments and cannot in general be extrapolated to more heavily substituted fragments. However, we are using them only to calculate differences, *e.g.* in J^t between the C·CHCl·CHCl·C fragment of (1) and the $CHCl_2{\cdot}CHCl{\cdot}C$ fragment of (2A) and for this purpose they should be reasonable approximations.

[22] R. J. Abraham and G. Gatti, *J. Chem. Soc.* (*B*), 1969, 961.

[23] W. F. Reynolds and D. J. Wood, *Canad. J. Chem.*, 1969, **47**, 1295.

equations in four unknowns and furthermore these equations are not independent. Eliminating $(n_C + n_D)$ from equations (2) and (3) by the use of (4) gives, from (1) and (4), equation (5) and from (2) and (4), (6). Thus provided only that the

$$J_{1a,2} - J_g' = (J_t - J_g')(2n_A + n_B)/2 \qquad (5)$$

$$J_t - J_{1b,2} = (J_t - J_g)(2n_A + n_B)/2 \qquad (6)$$

couplings of (4B) are the averages of those of (4A, C, and D), then equations (2) and (3) are not independent. However, the values of the couplings may be tested by equations (5) and (6) as the answers should be identical. Using the above rotamer couplings with the observed couplings in n-pentane (Table 1) gives $2n_A + n_B$ 1·84 [equation (5)] and 1·88 [equation (6)] in excellent agreement. From these results and equation (4) we have $n_B = 1{\cdot}86 - 2n_A$ and $n_C + n_D = n_A - 0{\cdot}86$.

As however all the mole fractions are $\geqslant 0$, these equations define n_A as $0{\cdot}86 \leqslant n_A \leqslant 0{\cdot}93$ and thus the couplings alone provide surprisingly a reasonably well defined value of n_A and also therefore of n_B and $(n_C + n_D)$. In order to differentiate between n_C and n_D and also to further define n_A and n_B the dipole moment determination in the same solvent may be used, together with the calculated rotamer dipole moments (Table 2) and equation (7). This differentiates n_C and n_D as (4C and D) have very different dipole

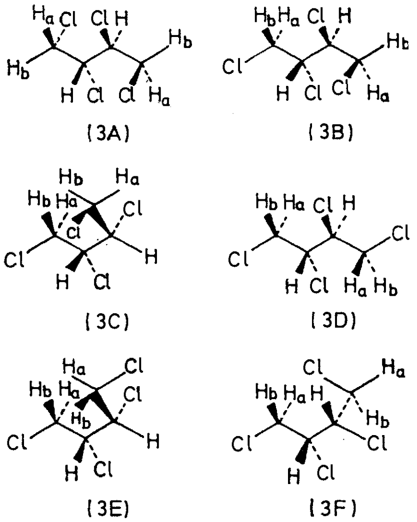
$$\mu^2 = \sum_i n_i \mu_i^2 \qquad (7)$$

moments. Introducing equation (7) with again the condition that all n_i are $\geqslant 0$, gives as final values n_A 0·86, n_B 0·14, n_C, n_D 0·0, with a calculated dipole moment of 1·02 D; *cf.* 1·18 D observed.

A similar analysis of the benzene solution results gives n_A 0·75, n_B 0·25, n_C, n_D $\leqslant 0{\cdot}02$ and these give μ_{calc} 1·36 D; *cf.* 1·46 observed.

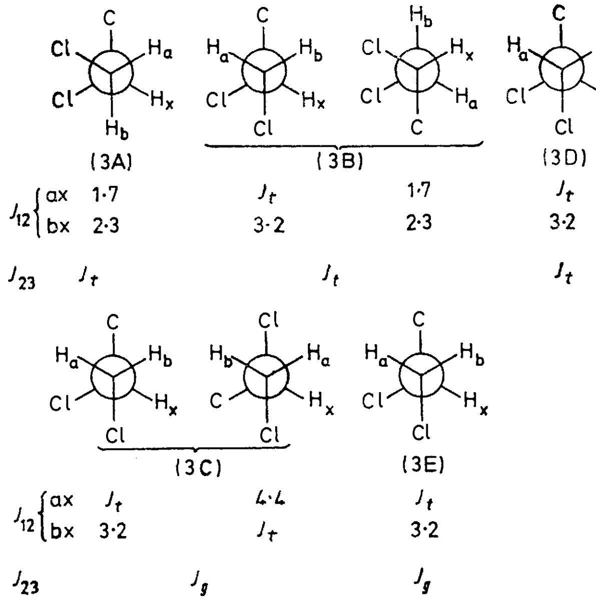
The relative rotamer energies obtained from these proportions (note that 4B has a statistical weight of two, whereas all the other rotamers have a statistical weight of one), are $E_B - E_A$ 1·5 (n-pentane) and 1·1 kcal mol^{-1} (benzene), with $E_C - E_A$ and $E_D - E_A \geqslant 2{\cdot}5$ kcal mol^{-1} in all solvents.

Compound (3).—This is the most complex system to consider, as the MODELS 2 calculations predict five populated rotamers (3A—E) (Table 2 and Scheme 2) of which the first three are of very similar energies. The most stable rotamer, (3A), has two *gauche*-couplings for the C(1) and C(2) protons and a *trans*-coupling for J_{23} and this is in agreement with the observed couplings (Table 1). This does not, however, provide an assignment of the methylene protons, and the values of the *gauche*-couplings in the C(1)C(2) fragment need to be estimated. The $CH_2Cl{\cdot}CHCl$ fragment is shown for the different rotamers in the Newman projections,* from which the rotamer couplings may be estimated in precisely the same way as for (4), *i.e.* from the observed couplings in similar fragments, *e.g.* $CH_2Cl{\cdot}CH_2Cl$, and correcting for the introduction of the carbon substituent. These values are given below, and as for (4) we take J_t 11·1 Hz for all the rotamers. Also of course the rotamer couplings for those rotamers [(3B and C)] with two different fragments are the averages over the C(1)C(2) and C(3)C(4) fragments giving values of J_{ax} and J_{bx} of 6·4 and 2·8 (3B) and 7·8 and 7·2 Hz (3C). The populated rotamers have different values of J_{23} and here we take values of J_t and J_g for this fragment obtained previously from (1) and (2) of 10·1 and 1·4 Hz.



SCHEME 2 Populated rotamers of *meso*-$CH_2Cl{\cdot}CHCl{\cdot}CHCl{\cdot}CH_2Cl$ (3)

The assignment of the observed couplings of the CH_2Cl group to H_a and H_b is not immediately obvious as the most stable rotamer, (3A), has two *gauche*-couplings of similar magnitudes. However (3B), the next most stable rotamer,



has $J_{ax} \gg J_{bx}$ and this provides the basis for the assignments of the larger coupling to J_{ax}. The third most populated rotamer, (3C), has $J_{ax} \approx J_{bx}$, but also would not be expected to make a major contribution as the observed value of J_{23} of 8·56 Hz (CCl_4) strongly favours (3A and B).

This assignment is supported by the solvent dependence of the couplings in that on the basis of the solvation energies (Table 2) the percentage of (3C) is expected to decrease in polar solvents relative to (3A and B) and thus J_{23} will increase and J_{bx} decrease as observed (Table 1). The value

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[*] The assignment of the equivalent methylene protons on the C(1)C(2) and C(3)C(4) fragments follows from the molecular centre of symmetry for the symmetric rotamers 3A and 3D and by rotation from these for the less symmetric rotamers.

of $J_{\rm ax}$ will however depend on the relative proportions of (3A and B) which may not be constant (see later).

Even with the assignments and the values of the rotamer couplings obtained there are four equations (three observed couplings plus the summation) and five unknowns ($n_{\rm A} - n_{\rm E}$) and thus the general solution is ill defined. One simple treatment which is now not based on the calculated energies is to disregard the two high energy rotamers (3D and E). It is now possible to solve for $n_{\rm A}$, $n_{\rm B}$, and $n_{\rm C}$ from the observed couplings. Indeed as there are four equations in three unknowns these are overdetermined and thus provide a check of the original assumption. From the couplings in CCl_4 solution, the equations for $J_{\rm ax}$ and J_{23} were solved to give $n_{\rm A}$ 0·57, $n_{\rm B}$ 0·26, and $n_{\rm C}$ 0·18 and these give $J_{\rm bx}$ 3·3 Hz; *cf.* 3·68 observed. For the CH_3CN solution the corresponding values are $n_{\rm A}$ 0·46, $n_{\rm B}$ 0·38, and $n_{\rm C}$ 0·15 giving $J_{\rm bx}$ 3·25 Hz; *cf.* 3·17 observed.

The solution of the four equations in terms of five rotamers is not completely undefined as of course there is always the condition that all n_i must lie between 0 and 1. It is therefore possible to obtain ranges of values for the five unknowns. These are, for CCl_4 solution, $n_{\rm A}$ 0·57—0·65, $n_{\rm B}$ 0·24—0·08, $n_{\rm C}$ 0·19, $n_{\rm D}$ 0·0—0·08, and $n_{\rm E}$ 0·0 giving calculated couplings of 3·98 ($J_{\rm ax}$), 3·35 ($J_{\rm bx}$), and 8·45 (J_{23}).

For acetonitrile solution the corresponding figures are $n_{\rm A}$ 0·51—0·68, $n_{\rm B}$ 0·33—0·0, $n_{\rm C}$ 0·08, $n_{\rm D}$ 0·0—0·19, and $n_{\rm E}$ 0·07, giving calculated couplings of 4·44 ($J_{\rm ax}$), 2·96 ($J_{\rm bx}$), and 8·76 (J_{23}).

The two treatments are in reasonable agreement, showing that the proportions of (3D and E) are in general small. Note that some of the populations are linked in that as $n_{\rm B}$ increases $n_{\rm D}$ decreases and similarly for $n_{\rm C}$ and $n_{\rm E}$.

The relative rotamer energies obtained from the above figures [note that (3B and C) have statistical weights of two, the others of one] are for CCl_4 solution, $\Delta E({\rm B} - {\rm A})$ 1·0, $\Delta E({\rm C} - {\rm A})$ 1·1, $\Delta E({\rm D} - {\rm A})$ *ca.* 2·3, $\Delta E({\rm E} - {\rm A})$ $>2·5$ kcal mol^{-1} and for acetonitrile solution the corresponding values are 0·7, 1·2, 1·7, and 2·0 kcal mol^{-1} respectively.

DISCUSSION

The preceding section has shown that the observed couplings and dipole moment can be analysed with the aid of the calculations to obtain in all cases estimates of the rotamer populations. However the calculations have so far only been used qualitatively, *i.e.* to identify the stable rotamers, *etc.* It is therefore of interest to compare the observed and calculated rotamer energies.

There are two separate comparisons to be made. The vapour phase rotamer energies may be directly compared with the MODELS 2 results and the change with solvent with the DIPQUADMOMS results, as these two theories, although used in conjunction are entirely independent.

The vapour-phase rotamer energy differences ($\Delta E^{\rm V}$) may be obtained from the observed energy differences in the various solvents from the fact that the solvation energy of any rotamer in pentane is about one-third that in acetonitrile (Table 2). The vapour state energy differences obtained in this way are given in Table 3, together with the calculated values. Also the change in the relative rotamer energies ($\delta\Delta E$) from the vapour to the two solvents studied is also given in Table 3, together with the calculated values.

It can be seen that the MODELS 2 calculations overestimate the rotamer energy differences in the hexachlorobutane (2) and possibly (1), but in contrast the calculated values for the tetrachlorobutanes (3) and (4) are generally smaller than observed. Part of the error for (2) could lie in errors in the treatment (see later), but the overestimate for the sterically crowded hexachlorobutanes has an obvious explanation in that the calculations are based on a standard geometry. Increasing all the $\widehat{\rm CCC}$ angles from 111 to 112·5° (a better value for a carbon chain), did not have any appreciable effect. Obviously in such sterically crowded molecules relaxation of *all* the angles will occur and this will decrease all the rotamer energies, and tend therefore to decrease the relative rotamer energies, as observed.

TABLE 3

Observed and calculated rotamer energies [a] (kcal mol^{-1}) for chlorobutanes

			$\delta\Delta E^{\rm S}$			
	$\Delta E^{\rm V}$		$\varepsilon = 1·8$		$\varepsilon = 37·5$	
Rotamer	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
(1B)	$>2·5$	5·2		$-0·1$		0·1
(2B)	1·8	4·7	0·2	0·6	0·6	2·4
(3B)	1·2	0·3	0·2	0·0	0·5	0·4
(3C)	1·1	0·3	0·0	$-0·4$	$-0·1$	$-0·2$
(3D)	$\sim2·3$	0·9	0·3	0·3	0·6	0·8
(3E)	$>2·5$	0·9		0·3		1·0
(4B)	1·9	0·9	0·4	0·2	0·8 [b]	1·1
(4C, D)	$>2·5$	1·2		0·6		2·1

[a] Relative to the most stable rotamer (A) in all cases.
[b] Benzene solution.

The situation for (3) and (4) is less obvious, as here the rotamers are not sterically crowded. The observed and calculated energies are indeed in reasonable agreement except that the most stable rotamer in both compounds is *ca.* 1 kcal mol^{-1} more stable than calculated. (This of course affects all the values in Table 3.) The calculations appear to underestimate consistently the destabilising affect of a chlorine atom in a *trans*-C·C·C·Cl relationship (Schemes 1 and 2) by *ca.* 0·5—1·0 kcal mol^{-1}. However, this may not be the only factor involved and further investigation is needed to confirm this.*

The solvation energy calculations for (3) and (4), in which of course the precise geometry is not so critical, are in very reasonable agreement with the observed energies (Table 3), but there is an outstanding discrepancy for (2) in which (2B) is predicted to be much more stabilised by polar solvents than is observed. Some of this could be due to errors in the treatment as in this case one rotamer is predominant and thus the rotamer energies become critically dependent on the estimated values of the rotamer couplings. (In this case the observed values of the couplings in n-pentane solution of 9·20 and 1·98 Hz, are only *ca.* 0·5 Hz different from those estimated for the most stable rotamer of

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* *Note added in proof.* Our recent calculations show that this effect can be reproduced by relaxation of the C·C·C angles for *each* rotamer.

9·64 and 1·36 Hz.) Any closing of this small gap would result in both ΔE^V and the solvation energy ($\delta\Delta E$) increasing, which is what is predicted. However, there is no good reason for changing the estimated rotamer couplings and the discrepancy may also arise from limitation in the solvent theory due to well separated dipolar groups.

The general agreement in Table **3** is however very reasonable and suggests that such calculations, when used in conjunction with physical measurements can provide a powerful method of determining rotamer populations in more complex molecules than have hitherto been accessible.

After the manuscript had been prepared, we were informed of the results of a detailed study of (3) and (4) mainly by i.r. spectroscopy.[24] It is most encouraging to note that the conclusions of this work as to the most stable rotamers and likely higher energy rotamers are essentially identical with our results.

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[24] A. B. Dempster, K. Price. and N. Sheppard, unpublished results.