Conformational Equilibria and Barriers to Rotation in Monohalogenobutanes with Methyl Substituents. Methyl–Halogen Interactions. The Size of a Halogen Atom

By **J. Edgar Anderson,* Christopher W. Doecke,** and **Harry Pearson,** Ralph Forster Laboratory of Organic Chemistry, University College, Gower Street, London WC1E 6BT

An n.m.r. study of barriers to rotation and conformational equilibria in 2-halogeno-2,3,3-trimethylbutanes and 2-halogeno-2,3-dimethylbutanes is reported. Results are discussed in terms of the steric requirement of halogen atoms, and the interaction of these atoms with adjacent methyl groups.

THE classical interactions of conformational analysis are the *gauche*, *trans*, and eclipsed 1,2-interactions along a carbon–carbon single bond, and the *cis* 1,3-interaction or parallel 1,3-interaction such as that of axial substituents on alternate atoms in a six-membered ring.

The interactions of halogen atoms in these conformational situations are of interest since much of what is known of intra- and inter-molecular interactions comes from the study of conformational equilibria in polyhalogenoethanes and their solvent dependence. An attraction of halogen substituents is that they may be considered as spherically symmetrical, but this is a deceiving assumption for while hydrogen, fluorine, and chlorine have successively greater conformational effects, those of bromine and iodine are often not much larger than that of chlorine (see Table 1).

TABLE 1

Conformational effects of halogen atoms (kcal mol^{-1})

	H	F	Cl	Br	I	Reference
Barrier to rotation in CH_3–CH_2X	2.88	3.33	3.68	3.68	3.2 ± 0.5	3
A Value. Free energy difference between axial and equatorial cyclohexyl halide. Axial is less stable	0	0.28	0.53	0.48	0.47	4
Gas-phase enthalpy difference between *gauche*- and *trans*-$CH_3CH_2CH_2X$. Less stable is X and CH_3 *trans*	0	0.5	0—0.6	0.1—0.5	0 ± 0.5	5—9
Liquid-phase enthalpy difference between *gauche*- and *trans*-$(CH_3)_2CHCH_2X$. Less stable is H and X *trans*	0		0.37	0.26	0.36	10, 11
Liquid-phase enthalpy difference between *gauche*- and *trans*-$CH_3CH_2C(CH_3)_2X$. Less stable is X and CH_3 *trans*	0		0.36	0.38	0.69	12

Another aspect of the interest of halogen atoms is illustrated by the third entry in Table 1, the propyl halides. While for n-butane the *trans*-conformation is more stable [1,2] by *ca.* 700 cal mol^{-1}, in the propyl halides the conformation with the halogen atom and methyl group *gauche* is preferred.[5-9] Szasz has suggested [13] that the CH_3–C bond has a group dipole with the CH_3 positive, and that interaction of this with the C–X bond whose dipole is in the opposite sense is the stabilising force counterbalancing the expected steric repulsion of the *gauche*-conformation. This has been discussed by Wilson.[14]

It is interesting to speculate whether conformational equilibria in the various series of butyl halides can be predicted from two generalisations suggested above, *viz.* that methyl–methyl *gauche*-interactions are destabilising (of a magnitude *ca.* 0.7 kcal mol^{-1} as for butane) and methyl–halogen *gauche*-interactions are stabilising (by *ca.* 0—0.5 kcal mol^{-1}). We report on the conformational equilibrium in the series of compounds (1), and barriers to rotation in series (2) and discuss these in terms of the above two hypotheses. We will also discuss the *relative* effects of halogen atoms. Fluorine atoms sometimes have exceptional effects, and for the others we will show and rationalise two kinds of situation, depending on whether the conformational effect of the halogen atoms is similar or changes markedly along the series chlorine to iodine.

We believe there is much to be gained by considering halides of types (1) and (2) with one halogen atom, and otherwise only carbon and hydrogen atoms. The

---

[1] P. B. Woller and E. W. Garbisch, jun., *J. Amer. Chem. Soc.*, 1972, **94**, 5310.

[2] G. J. Szasz, N. Sheppard, and D. H. Rank, *J. Chem. Phys.*, 1948, **16**, 704.

[3] Values are taken from a compilation, J. P. Lowe, *Progr. Phys. Org. Chem.*, 1968, **6**, 1, where original references are cited.

[4] F. R. Jensen, C. H. Bushweller, and B. H. Beek, *J. Amer. Chem. Soc.*, 1969, **91**, 344.

[5] E. Hirota, *J. Chem. Phys.*, 1962, **37**, 283.

[6] T. N. Sarachman, *J. Chem. Phys.*, 1963, **39**, 469.

[7] Y. Morino and K. Kuchitsu, *J. Chem. Phys.*, 1958, **28**, 175.

[8] N. Sheppard, *Adv. Spectroscopy*, 1959, **1**, 295.

[9] S. Armstrong, *Appl. Spectroscopy*, 1969, **23**, 575. There is no explicit determination of the proportion of isomers in n-propyl bromide and iodide in this report. Pictures of their microwave spectra at low resolution suggest that there are comparable amounts of both conformations present.

[10] E. Wyn-Jones and W. J. Orville-Thomas, *Trans. Faraday Soc.*, 1968, **64**, 2907.

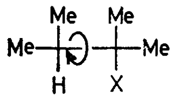
[11] A. Honeix, G. Martin, and M. Queneudec, *J. Mol. Structure*, 1968, **3**, 369.

[12] P. J. D. Park and E. Wyn-Jones, *J. Chem. Soc.* (*A*), 1968, 2944.

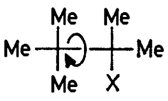
[13] G. J. Szasz, *J. Chem. Phys.*, 1955, **23**, 2449.

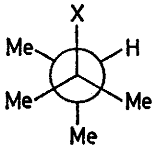
[14] E. B. Wilson, *Chem. Soc. Rev.*, 1972, **1**, 293.

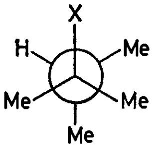
substantial solvent and conformation dependent interactions of polyhalogenated compounds are avoided.

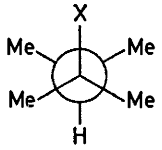

(1)

a ; X = H
b ; X = F
c ; X = Cl
d ; X = Br
e ; X = I


(2)


(3)


(4)


(5)

RESULTS

Of compounds (1a—e) only (1c—e) show temperature-dependent n.m.r. spectra which can be associated with hindered rotation about the central bond. For example in the spectrum of (1d) the singlet for the two methyl groups on the carbon bearing the bromine atom becomes three lines of relative intensities 1 : 4.33 : 1 at −131.5°. The signal for the other two methyl groups is a doublet (due to coupling with the methine hydrogen) at room temperature, and appears as three overlapping doublets of approximately the same relative intensities at low temperature. The multiplet for the methine hydrogen becomes a complex multiplet at low temperature.

These changes are due to rotation about the central bond in (1) becoming slow on the n.m.r. timescale, when separate signals for *gauche*-isomers (3) and (4) and the *trans*-isomer (5) are observed. The two *gauche*-conformations (3) and (4) have identical spectra, but in either, the two methyl groups on one carbon atom are different thus it is the *gauche*-conformation that gives the two signals of equal intensity reported above. In the *trans*-conformation, methyl groups on the same carbon atom are magnetically indistinguishable and these give rise to the signals of relative intensities 4.33 at low temperature. Similar results were observed for (1c) [15] and (1e), but for (1b) no significant changes were observed down to −155°. This implies a lower barrier to rotation in (1b), compared with (1c—e) which is in accord with observations in series (2). The spectrum of (1a) was not examined for similar reasons.

The determination of barriers to rotation in (1d—e) involves assumptions and uncertainties as we have already shown in detail [15] for (1c). We did not therefore measure barriers for (1d—e) but only the relative populations and stabilities of the conformations, and these are reported in Table 2.

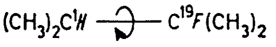
TABLE 2

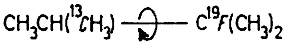
gauche- and *trans*-isomers of 2-halogeno-2,3-dimethylbutanes. Populations and enthalpy differences

Compound and substituent		T/K	*trans*-Conformation (%)	k_T = *trans*/*gauche*	ΔG_T [a]/ cal mol^{-1}	ΔH_0 [b]/ cal mol^{-1}
(1a)	H [c]	298	62	1.63	290	700
(1b)	F [d]	140	17	0.20	−450	−250
(1c)	Cl [e]	138	59	1.44	100	290
(1d)	Br [e]	141.5	68	2.13	210	410
(1e)	I [e]	141.5	88	7.33	560	760

[a] $\Delta G_T = 2.303RT\log k_T$, T as in column 2. A more positive value indicates that the *trans*-form is relatively more stable. [b] From ΔG_T assuming $\Delta S_0 = +1.376$ cal mol^{-1} K^{-1}. A more positive value indicates that *trans* is more stable. [c] Based on measurements of refractive index.[21] [d] By extrapolation of results in the temperature range 155—320°, and assuming *trans*- and *gauche*-coupling constants. See text. [e] By direct observation of n.m.r. signals from each isomer.

We sought information on the populations of conformers in the fluoro-compound (1b) from the carbon–fluorine stretch absorptions in the i.r. region [16] but this method is less direct and less sensitive than the n.m.r. coupling constant method using the dependence of these parameters on the dihedral angle between vicinal groups. In this case we used both the ^{1}H–^{19}F vicinal coupling shown in (6) and the ^{13}C–^{19}F vicinal coupling shown in (7).


(6)


(7)

For ^{1}H–^{19}F coupling we used model values of 2 and 44 Hz for the *cis*- and the *trans*-coupling constants.[17,18,*] The observed coupling constant is presumed to be a weighted mean of these two values and so yields the population of the two conformations and hence the equilibrium constant at a series of temperatures as shown in Table 3. A plot of log k against $1/T$ yielded an enthalpy difference between isomers of −207 cal mol^{-1} and an entropy difference of 1.7 cal mol^{-1} K^{-1}. The results in Table 2 for the fluoride are calculated from an extrapolation of the above plot. Using values of $J_{gauche} > 2$ Hz reduces the calculated proportion of the *trans*-isomer and gives a more negative ΔG_0 and ΔH_0.

The ^{13}C–^{19}F vicinal coupling constant was measured at 28, −10, and −60° and was found to be 6.2, 6.4, and 6.5 Hz respectively. That these are less sensitive is not surprising

---

[*] Ref. 17*a* reports that for *cis*-4-t-butylcyclohexyl fluoride, the axial fluorine atom shows coupling of 44 and 10 Hz to neighbouring *trans*- and *gauche*-hydrogens. For the *trans*-isomer, the *gauche*-coupling is unresolved. In cyclohexyl fluoride at −87°, it is concluded [18] that gauche coupling of the fluoride, be it axial or equatorial is <4 Hz.

[15] J. E. Anderson and H. Pearson, *J.C.S. Perkin II*, 1973, 960.

[16] A discussion of the problems involved in quantitative analysis using i.r. spectra which we used as our guide is given in R. T. Conley 'Infrared Spectroscopy,' Allyn and Bacon, Boston, 1972, ch. 6.

[17] (*a*) E. L. Eliel and R. J. L. Martin, *J. Amer. Chem. Soc.*, 1968, **90**, 682; (*b*) K. L. Williamson, Y.-F. L. Hsu, F. H. Hall, S. Swager, and M. S. Coulter, *J. Amer. Chem. Soc.*, 1968, **90**, 6717.

[18] F. A. Bovey, E. W. Anderson, F. P. Hood, and R. L. Kornegay, *J. Chem. Phys.*, 1964, **40** 3099.

since each is weighted average of four rather than two couplings as in the $^1H-^{19}F$ case. There are as yet no suitable models for relating $^{13}C-^{19}F$ vicinal coupling constants to dihedral angle, the most relevant data we can find being that in 1,1-difluorocyclohexane the *trans*- and *gauche*-coupling constants of carbons 3 and 5, to the fluorines are *ca.* 9.5 and 0 Hz respectively.[19]

TABLE 3

Temperature dependence of $^3J_{F-H}$ in (1b) and *gauche–trans*-equilibrium

T/°C	J_{H-F}/Hz	*trans* (%) [a]	$k = p_{trans}/p_{gauche}$
47.5	11.8	23.3	0.304
27	11.5	22.6	0.292
−35.5	11.1	21.7	0.277
−62.8	10.5	20.2	0.254
−95	10.1	18.3	0.239
−113.5	9.5	17.9	0.218
−118.0	9.4	17.6	0.214

[a] Based on the assumption that for 100% *trans* and 0% *trans* J_{H-F} is 44 and 2 Hz respectively. See text.

The striking result suggested by the coupling constant measurements is that for (1b) the preferred conformation is that with H and F *gauche* in contrast to the result for the other halides (see ΔH_0 values in Table 2).

The result for (1a) is that given by Mann and his co-workers [20] based on measurements of refractive indices. Ultrasonic determinations [21] suggest that there is rather less of the *gauche*-isomer present.

There are two *gauche*-conformations of equal energy for (1a—e). Otherwise the symmetry number of *gauche*- and *trans*-conformations is the same and for lack of better information it is assumed that there are no other factors contributing to a difference in entropy between conformations. Thus the enthalpy differences shown in Table 2 are calculated from the ΔG_0 values at 140 K assuming an entropy difference of 1.38 cal mol^{-1} K^{-1}.

The n.m.r. spectra of (2a—e) are temperature dependent, the singlet observed for the t-butyl signal of these compounds at room temperature becoming a 2 : 1 doublet at temperatures below *ca.* −100°. Thus at the low temperature, rotation about the central bond is slow on the n.m.r. timescale. Treatment of these temperature-dependent n.m.r. spectra in standard ways outlined elsewhere [22] leads to barriers to rotation about the central bond, typical values of which are shown in Table 4. Further information including rates of rotation at various temperatures is given in the Experimental section. These results have been reported in preliminary form.[23]

TABLE 4

Barriers to rotation in 2-halogeno-2,3,3-trimethylbutanes

	(2a)	(2b)	(2c)	(2d)	(2e)
H	H	F	Cl	Br	I
$\Delta G^‡$/kcal mol^{-1} [a]	6.97	8.04	10.43	10.73	11.14
$\Delta\Delta G^‡$/kcal mol^{-1}	0	1.1	3.5	3.8	4.2

[a] Typical values. See Experimental section for values over a range of temperatures.

DISCUSSION

Any discussion of the conformational equilibrium in monohalogenoethanes with otherwise only methyl substituents involves the series of compounds (8)—(13). In (8), (9), (11), and (13), each carbon of the carbon–carbon bond in question has two substituents of one kind and a unique substituent. '*Gauche*' refers to that conformation with the two unique substituents *gauche*, similarly *trans*. Interactions other than *gauche* halogen–methyl, halogen–hydrogen, and methyl–methyl are probably negligible.

$CH_3CH_2\cdot CH_2X$ **(8)**

$(CH_3)_2CH\cdot CH_2X$ **(9)**

$CH_3CH_2\cdot CH(CH_3)X$ **(10)**

$CH_3CH_2\cdot C(CH_3)_2X$ **(11)**

$(CH_3)_2CH\cdot CH(CH_3)X$ **(12)**

$(CH_3)_2CH\cdot C(CH_3)_2X$ **(13)**

X = Halogen or H

Chlorides, Bromides, and Iodides.—The n-propyl halides (8) were mentioned in the Introduction [5-9] and are shown in Table 1. Repulsion of *gauche*-methyl and halogen atoms might be expected at first sight, but the fact that there are comparable amounts of *gauche*- and *trans*-isomers suggests that there must be some attractive interaction between these groups balancing any steric effect. The other possibility, that hydrogen and halogen repel each other, seems unlikely.

The isobutyl halides (9) present a contrast since the *gauche*-conformation is more stable than the *trans* by a small amount,[10,11] although the latter has one more *gauche*-methyl–halogen interaction. Thus in contrast to series (8) steric repulsions of *gauche*-methyl and halogen groups are greater than any attractive interactions, but not by much since the energy difference between the two conformations is small in each case.

In series (11) the chloride, bromide, and iodide have been studied by i.r. spectroscopy.[12] The results are shown in Table 1. Once again, the preferred of the two possible conformations is that with methyl groups *trans*, and one of them *gauche* to a halogen atom.

In series (10) there are three possible conformations about the central bond. For the chloride, bromide, and iodide there is a slight preference for a conformation with the halogen *gauche* to a methyl group and the two methyl groups *trans* to each other.[24] There is no conclusive information on series (12).[25]

---

[19] D. Doddrell, C. Charrier, and J. D. Roberts, *Proc. Nat. Acad. Sci., U.S.A.*, 1970, **67**, 1649.

[20] G. Mann, M. Muhlstadt, J. Brabant, and E. Doring, *Tetrahedron*, 1967, **23**, 3393.

[21] (*a*) J. H. Chen and A. A. Petraukis, *J. Chem. Phys.*, 1959, **30**, 304; (*b*) J. Lamb *Z. Elektrochem.*, 1960, **64**, 135.

[22] J. E. Anderson and H. Pearson, *J. Chem. Soc.* (*B*), 1971, 1209.

[23] J. E. Anderson and H. Pearson, *Tetrahedron Letters*, 1972 2779.

[24] E. Benedetti and P. Cecili, *Spectrochimica Acta*, 1972, **28A**, 1007.

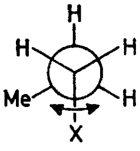
[25] F. F. Bentley and N. T. M. Devitt, *Spectrochimica Acta*, 1964, **20**, 105.

Finally, the present results on series (1) which is the series (13) suggests that except for the fluoride the *trans*-conformation is more stable than the *gauche*. The experimentally more stable conformation is that which has fewer methyl–methyl *gauche* interactions and more halogen–methyl *gauche*-interactions, in accord with what has come to be expected from the results of series (8)—(12). In this series there is a gradual but small increase in preference for the *trans*-conformation along the series of halides.

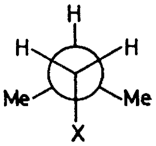
Of compounds (8—13; X = H) without a halogen substituent only (10; X = H) and (13; X = H) [=(1a)] have given clear results,[1,2,20,21b] namely that the preferred conformation is that with fewer *gauche* methyl–methyl interactions.

The weight of evidence does suggest that ethanes with one chlorine, bromine, or iodine atom and otherwise only one or more methyl groups as substituents will choose that conformation with fewest methyl–methyl *gauche*-interactions and most methyl–halogen *gauche*-interactions. However a methyl–methyl *gauche*-interaction is known to have ΔG *ca.* 0.7 kcal mol^{-1} and this alone can explain the results in series (10)—(13) provided the nett *gauche*-interaction of methyl and halogen (*i.e.* the combined steric and polar interaction *) is close to zero. This requires the attractive interaction between methyl and halogen to be of the same size as the steric repulsion one would expect at first glance, and it is here that series (8) and (9) are important for there are no methyl–methyl *gauche*-interactions.

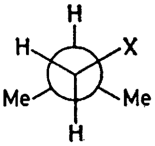
The striking fact coming from a comparison of these series is that the favourable *gauche*-methyl–halogen interaction [see (14)] which explains the result for (8) suggests that the preferred conformation in series (9) is (15) whereas experimentally it is observed [1,2] to be (16).



(14)



(15)



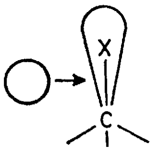
(16)

In conformation (15) of series (9) any rotation to allow X to reach its optimum dihedral angle with respect to one methyl group moves X away from its optimum dihedral angle with respect to the other methyl group. In conformation (16) rotation can take X to its optimum dihedral position with respect to the *gauche*-methyl group without much affecting its interactions with the other remote methyl group. It may be for this reason that (16) or its mirror image is preferred. Further, in (15) steric repulsion will be about double compared with (16) yet since the dipole of the C–X bond is the same, dipole–dipole attraction will not be increased to a similar degree. In other words we conclude that conformational effects need not be additive!

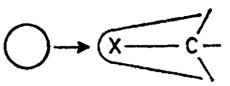
The other fact that obtrudes from each of these series and from the barriers to rotation in series (2) is that the results for chlorine, bromine, and iodine are remarkably similar. Berlin and Jensen have suggested [26] that such similarities reflect the fact that the increase in the van der Waals radius of the halogen is offset by the increase in the polarisability of the carbon–halogen bond which may be considered as a measure of the ease with which the electron cloud around the halogen nucleus can be distorted. These two factors are not, of course, independent of each other.

It should also be remembered that halogen bond lengths are different so the position of the halogen atom with respect to the rest of the molecule changes. In the case of fluorine they consider quite reasonably that the small van der Waals radius is much more important than the low polarisability, so the conformational effect is low.

There are however conformational situations as shown below in which the effect of a halogen atom increases quite dramatically down the series and we would like to offer an explanation of this. When the conformational effects of chlorine, bromine, and iodine are of a similar size, the interactions giving rise to the effect are lateral, and can be accommodated by polarisation along the C–X direction as in (17). Where the interaction is more end-on as in (18) the effect of the halogen increases markedly from chlorine to bromine to iodine. In this case polarisation of the electron cloud away from the interaction would be opposed by other groups attached to the carbon atom. There is no such opposition in (17), and the examples quoted in Table 1 and the dimethylbutyl and trimethylbutyl halides which are the subject of this report fall into this class.



(17)



(18)

Examples of situation (18) are not so well known and are worth illustrating. In the *ortho*-substituted benzyl halides (19), the barrier to rotation is expected to be determined by the interaction shown in (20). The barriers shown alongside were measured by Cupas *et al.*[27]

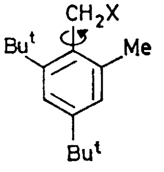
---

* We are aware of the danger of trying to separate interactions between groups into steric and polar parts. However, if groups are separated by less than the sum of their van der Waals radii, there is by definition some steric repulsion. Since they are nonetheless at a conformational equilibrium position, this repulsion is being balanced by something attractive in the absence of external influences. This attraction may be polar as suggested by Szasz.[2] Alternatively, if van der Waals radii are considered as infinitely variable, changing from each molecular situation, the justification for invoking steric and polar interactions is less.

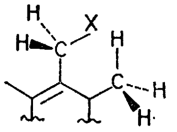
[26] A. J. Berlin and F. R. Jensen, *Chem. and Ind.*, 1960, 998.

[27] C. A. Cupas, J. M. Bollinger, and M. Haslanger, *J. Amer. Chem. Soc.*, 1968, **90**, 5502.

who noted the contrast in the geometry of the interaction to that in cyclohexane. In series (21) where the rotational transition state is shown, the barrier again changes appreciably.[28] The conformational inversion of the large ring in (22) requires the aliphatic chain to pass the halogen atom X. Here there are even larger changes in barrier with changes in the halogen atom.[29] Finally Lambert [30] has calculated that for (23) the free energy difference between axial and equatorial conformations increases greatly down the halogen series. The important interaction is again close to an end-on type (see (24)]. That end-on approach to a carbon–halogen bond produces greater interactions than lateral approach is a useful distinction which we have referred to elsewhere [23] as ' the anisotropy of the van der Waals radius.'

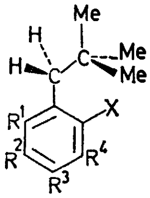


(19)



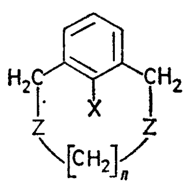
(20)

X=Cl $\Delta G^{\ddagger}$/kcal mol^{-1} 11·3
X=Br 12·5
X=I 15·4

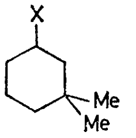


(21)

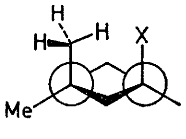
X=Cl $\Delta G^{\ddagger}$/kcal mol^{-1} 14·7
X=Br 16·6
X=I 18·8



(22)



(23)



(24)

Fluorides.—In the fluoride (1b) the *gauche*-conformation is of lower energy than the *trans*. In contrast to small halogen–methyl interactions of a few hundred cal mol^{-1} which we have postulated for other halides, we have to conceive in the *gauche*-conformation of (1b) an unusually large attractive interaction involving the fluorine, of the order of 1 kcal mol^{-1} more than balancing the unfavourable *gauche*-methyl–methyl interactions present in that conformation. This agrees well with the result for n-propyl fluoride. As with the other halides, this stabilising interaction seems to be less when the fluorine is simultaneously *gauche* to two methyl groups, presumably for the same reasons. There is thus no need to invoke a *unique* fluorine–hydrogen attractive interaction not found between hydrogen and other halogen atoms. The subject of attractive fluorine–hydrogen interactions has been much discussed recently.[31]

The barriers to rotation in the series (2) (see Table 4) fit well with the discussion above. The interactions in which the halogen atom is involved during rotation are lateral, hence the barrier, which increases markedly from (2a) to (2c) (X = H, F, then Cl) then increases by only a small amount for (2d and e) (X = Br, then I).

We have shown [32] that the barriers to rotation in (2a—e) are all unusually low due to *gauche*-methyl–methyl interactions in the ground state which are relieved somewhat during rotation. This contributes to the fact that the barrier in (2b) is the lowest we know for a hexasubstituted ethane, while that for (2e) is not particularly large for such molecules.[33]

Conclusions.—In the methyl-substituted propyl and butyl halides, methyl–methyl *gauche*-interactions are destabilising in comparison to methyl–hydrogen. Relative to halogen–hydrogen, halogen–methyl *gauche*-interactions can satisfactorily be considered as a combination of a destabilising steric interaction and a stabilising dipole–dipole interaction. These steric and dipolar interactions are of similar size and opposite sign for chlorine, bromine, and iodine, but for fluorine the attractive interaction is considerably greater than the repulsive one.

EXPERIMENTAL

N.m.r. spectra were measured on Varian HA100 and CFT20 spectrometers and barriers to rotation were calculated as described previously,[22] relative intensities of peaks being measured by planimeter.[15] Solutions were 0.1—0.2M in CF_2Cl_2 solvent.

The syntheses and n.m.r. spectra of compounds (2a),[33] (2c),[22] (2d),[33] and (1c) [15] have been described elsewhere.

2-*Fluoro*-2,3,3-*trimethylbutane* (2b).[34]—Dry HF gas was passed for *ca.* 2 min onto neat 2,3,3-trimethylbutene at −40°. Distillation and chromatography gave a white plastic *solid* which after molecular distillation from $MgSO_4$ had m.p. 24° (Found: C, 71.05; H, 12.85. $C_7H_{15}F$ requires C, 71.15; H, 12.8%), $\delta(CF_2Cl_2)$ 0.97 (9 H, d, J 0.75 Hz) and 1.28 (6 H, d, J 21 Hz). At −130°, the 9 H signal appears as a 1 : 2 doublet at δ 0.92 and 1.01. Rate constants for rotation were measured [22] (T/K, k/s^{-1}, $\Delta G^{\ddagger}$/kcal mol^{-1}): 147.5, 2.9, 8.12; 148.4, 3.9, 8.08; 149.4, 5.0, 8.07; 149.8, 6.0, 8.04; 152.4, 10.0, 8.02; 154.8, 18.0, 7.97; 155.4, 22.0, 7.94; 157.0, 25.0, 8.02; $\Delta H^{\ddagger}$ 9.9 kcal mol^{-1}, $\Delta S^{\ddagger}$ 12.2 cal mol^{-1} K^{-1}.

---

[28] B. Nilsson, P. Martinson, K. Osslon, and R. E. Carter, *J. Amer. Chem. Soc.*, 1974, **96**, 3190.

[29] F. Vogtle, *Tetrahedron*, 1970, **26**, 5299 and earlier work cited therein. In no one series of compounds were barriers obtained for all halides.

[30] D. S. Bailey, J. A. Walder, and J. B. Lambert, *J. Amer. Chem. Soc.*, 1972, **94**, 177.

[31] N. D. Epiotis, S. Sarkanen, D. Bjorkquist, L. Bjorkquist, and R. Yates, *J. Amer. Chem. Soc.*, 1974, **96**, 4075.

[32] J. E. Anderson and H. Pearson, *J.C.S. Chem. Comm.*, 1972, 908.

[33] J. E. Anderson and H. Pearson, *J. Amer. Chem. Soc.*, 1975, **97**, 764.

[34] A. D. Petrov, V. L. Suschinsky, and M. P. Stebanova, *Izvest. Akad. Nauk, S.S.S.R. Otdel. Khim. Nauk*, 1956, 510 (*Chem. Abs.*, 1965, **50**, 1665).

Compound (2e) was prepared from the corresponding alcohol and hydrogen iodide, m.p. 140° (sealed tube) (lit.,[35] 140—142°), δ(CF_2Cl_2) 1.16 (9 H, s) and 2.01 (6 H, s). At −110° the 9 H signal appears as a 1 : 2 doublet at δ 1.00 and 1.23. Rate constants for rotation were measured as for (2b): 203.3, 3.8, 11.21; 206.9, 7.1, 11.15; 210.0, 9.8, 11.19; 212.3, 14.9, 11.14; 215.8, 36, 10.96; 217.7, 53, 10.93; 219.5, 63, 10.91; 220.7, 84, 10.84; 226.4, 104, 11.04; 229.0, 147, 11.01; 232.1, 183, 11.07; 235.1, 260, 11.05; 238.4, 340, 11.09: $\Delta H^{\ddagger}$ 11.93 kcal mol^{-1}, $\Delta S^{\ddagger}$ 4.0 cal mol^{-1} K^{-1}.

Compound (1b) was prepared by a literature method.[36] At ambient temperature the methyls on the carbon bearing the fluorine atom appear as a doublet ($^3J_{H-F}$ 21 Hz) at δ 1.26, the isopropyl methyls appears as a doublet ($^3J_{H-H}$ 6.7 Hz) at δ 0.93 while the tertiary hydrogen is a complex multiplet at δ 1.85. There are no significant changes in the spectrum at −160°. In the i.r. spectrum peaks at 1 104 and 1 072 cm^{-1} were assigned to carbon–fluorine stretch vibrations in the *gauche-* and *trans*-isomers respectively. The relative intensities are 77 : 23 at ambient temperature and 68 : 32 at −76°.

Compound (1e) was prepared by addition of HI to 2,3-dimethylbut-2-ene, b.p. 53.6° at 17 mmHg (lit.,[37] 145°). At ambient temperature the methyl groups on the carbon bearing the iodine atom appear in the n.m.r. as a singlet at δ 1.92, while at −132° they appear as a 1 : 14.7 : 1 triplet at δ 20.03, 1.92, and 1.70. The chemical shifts of the hydrogen and of the methyl groups of the isopropyl group are very similar, at δ *ca.* 1.03, and have as a result a complex appearance. It appears, surprisingly compared with the other compounds of type (1), that the methine hydrogen signal is slightly upfield of that of the methyl hydrogens rather than considerably downfield. At −132° the spectrum of these hydrogens is different, but still too complex to analyse. In the i.r. the peaks at 537 and 571 cm^{-1} were assigned to carbon–iodine stretch vibrations in the *trans-* and *gauche*-isomers respectively. The relative intensities of these peaks were found to be 50 : 44 at 25° and 70 : 30 at −74°.

Compound (1c) and its n.m.r. spectra have been described previously.[15] In the i.r. spectrum peaks at 613 and 569 cm^{-1} (lit.,[38] 611 and 569 cm^{-1}) were assigned to carbon–chlorine stretch vibrations in the *gauche-* and *trans*-isomer respectively.[38] The relative intensities are 60 : 40 at 25° and 59 : 41 at −75°.

Compound (1d) was prepared by the addition of HBr to 2,3-dimethylbut-2-ene, b.p. 43° at 20 mmHg (lit.,[39] 59.3° at 62 mmHg). At ambient temperature the methyl groups on the carbon bearing the bromine atom appear in the n.m.r. as a singlet at δ 1.72, while at −131.5° they appear as a 1 : 4.3 : 1 triplet at δ 1.87, 1.79, and 1.63. The other methyl groups appear as a doublet at δ 1.06 (*J* 6.6 Hz) at ambient temperature and three doublets of *ca.* 1 : 4 : 1 relative intensity at δ 1.19, 1.04, and 0.92 respectively (*J* 6.6 Hz) at *ca.* −134°. The tertiary hydrogen appears as a multiplet (*J* 6.6 Hz) partially overlapping the former signal at δ 1.73 at ambient temperature. The signal could not be observed at low temperature. In the i.r., peaks at 545 and 587 cm^{-1} were assigned to carbon–bromine stretch vibrations in the *trans-* and *gauche*-isomers respectively. The relative intensities of these peaks were found to be 42 : 58 and 71 : 29 at 25° and −70°.

S.R.C. Studentships to H. P. and C. W. D. are gratefully acknowledged.

[5/1140 *Received, 11th June,* 1975]

---

[35] Butlerlow, *Annalen*, 1975, **177**, 184.

[36] K. Wiechart, C. Gruenert, and H. J. Preibisch, *Z. Chem.*, 1968, **8**, 64.

[37] G. Costello, G. D'Amato, and E. Biagini, *J. Chromatography*, 1969, **41**, 313.

[38] J. J. Shipman, V. L. Folt, and S. Krimm, *Spectrochimica Acta*, 1962, **18**, 1603.

[39] G. D. Harden and A. Maccoll, *J. Chem. Soc.*, 1957, 5028.