Molecular Polarisability: Conformations of Some Polar Substituted Ethanes

By Lawrence H. L. Chia, Eng Huang, and Hsing-Hua Huang,* Chemistry Department, University of Singapore, Singapore 10

The dipole moments and molar Kerr constants of 2,3-dichloropropene and 11 halogenated ethanes in carbon tetrachloride are analysed to yield information on the molecular distribution of the rotational isomers and values of the dihedral angles between the polar groups.

SUBSTITUTED ethanes with two halogens (or other polar groups) attached to the 1- and 2-positions are molecules whose molar Kerr constants can be expected to show a sensitive dependence on the conformations adopted during rotation about the central C–C bond. Here, we report a study of the molecular conformations for carbon tetrachloride solution of 11 such ethanes and the related molecule 2,3-dichloropropene, based on considerations of molecular polarity and polarisability.

EXPERIMENTAL

The compounds studied are listed in Table 1.

The meso- and racemic 2,3-dichlorobutanes and racemic 2,3-dibromobutane were prepared by halogenation of the appropriate but-2-ene.[1,2] The purity of these as well as the other (commercial) samples were determined by g.l.c., refractive index measurements, and microanalyses, after fractional distillation under reduced pressure.

Apparatus.—Standard procedures were adopted for the measurement of the dielectric constants,[3] densities,[4] refractive indices,[4] and electric birefringences[5] for carbon tetrachloride solutions at 25°.

pure liquids[6] (1·75 and 1·63 D respectively) while the values for the other compounds may be found in McClellan's compilation[7] or in the references indicated: 1,2-dichloropropane,[8] 1,2-dibromopropane,[9] 2,3-dibromo-2,3-dimethylbutane,[9,10] 1,2-dichloro-2-methylpropane,[11] and 2,3-dichloropropene.[12a]

The molar Kerr constants of the compounds reported in Table 1 have not been recorded before. Although those of the racemic compounds are not known, no attempt was made to measure them.

RESULTS

The dielectric and electric birefringence results are summarised in Table 1. Table 2 gives a summary of calculations on theoretical molar Kerr constants. Details of the experimental results together with those of calculated molar Kerr constants for various conformations, can be obtained from Supplementary Publication SUP No. 20660 (21 pp., 1 microfiche).†

DISCUSSION

All the meso-compounds can be expected to exist in solution as mixtures of trans- and gauche-rotamers in

TABLE 1

Polarisations, refractions, dipole moments, and molar Kerr constants at infinite dilution at 25 °C

	$\alpha\varepsilon_1$	β	γ	δ	P_2 (cm^3)	R_D (cm^3)	R_D (calc.)	μ_D(D) [a]	$10^{12}{}_\infty({}_mK_2)$
meso-2,3-Dichlorobutane	3·91	−0·437	−0·027	21·8	86·0	30·3	30·3	1·63 ± 0·04 [b]	24 ± 1 [b]
(±)-2,3-Dichlorobutane	4·78	−0·411			97·2	29·9	30·3	1·79 ± 0·05	
meso-2,3-Dibromobutane	1·91	0·107	0·049	19·8	78·8	36·6	36·1	1·41 ± 0·04	38 ± 1
(±)-2,3-Dibromobutane	1·71	0·117			74·0	36·8	36·1	1·32 ± 0·02	
1,2-Dichloropropane	3·50	−0·377	−0·032	22·4	70·3	25·6	25·7	1·46 ± 0·03	22 ± 1
1,2-Dibromopropane	1·23	0·177	0·053	8·4	56·7	32·0	31·4	1·06 ± 0·04	15·5 ± 0·5
1-Chloro-2-cyanoethane	22·48	−0·394	−0·030	228·9	235·9	20·6	20·6	3·29 ± 0·05	174 ± 6
1-Bromo-2-cyanoethane	14·50	0·043	0·029	140·7	229·3	23·3	23·5	3·16 ± 0·03	160 ± 7
2,3-Dibromo-2,3-dimethylbutane	0·75	0·041	0·058	12·8	62·2	44·8	45·4	0·86 ± 0·08	29 ± 1
1,2-Dichloro-2-methylpropane	3·46	−0·461	−0·037	24·9	80·6	30·4	30·3	1·54 ± 0·04	28 ± 1
2,3-Dichloropropene	4·51	−0·323		37·4	80·0	25·1	25·2	1·62 ± 0·04	36 ± 1

[a] μ is calculated assuming that $_DP = 1·05\ R_D$. [b] The uncertainties in the values for μ$_D$ and $10^{12}{}_\infty({}_mK_2)$ are estimated probable errors.

Previous Measurements.—The dipole moments of meso-2,3-dichlorobutane, racemic 2,3-dichlorobutane, 1-chloro-2-cyanoethane and 1-bromo-2-cyanoethane have not been reported before. Those of 2,3-dibromobutane (meso and racemic) have been determined from measurements on the

† For details of Supplementary Publications see Notice to Authors No. 7 in J. Chem. Soc. (A), 1970, Issue 20.

dynamic equilibrium. Similar equilibria will apply in the case of the racemic compounds although a different variety of rotational isomers will be involved.

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TABLE 2

Calculated dipole moments and molar Kerr constants with corresponding *gauche* percentage population (X) [a] for various values of the dihedral angle (θ)

meso-2,3-Dichlorobutane

	(cis)					(trans)
$\theta\ (°)$	0	60	70	75	80	180
$\mu(D)$	3·25	2·82	2·66	2·58	2·49	0
$X\ (\%)$	25·0	35·4	37·3	39·7	42·7	
$10^{12}{}_m K$	229·4	109·4	72·1	58·1	45·0	3·2
$X\ (\%)$	9·2	19·7	30·3	38·0	50·0	

meso-2,3-Dibromobutane

$\theta\ (°)$	0	60	70	80	85	180
$\mu(D)$	3·48	3·01	2·85	2·67	2·57	0
$X\ (\%)$	16·4	21·9	24·5	28·0	30·2	
$10^{12}{}_m K$	497·7	223·1	157·2	113·8	73·0	24·7
$X\ (\%)$	5·7	13·1	19·0	26·9	44·3	

1,2-Dichloropropane

$\theta\ (°)$	0	50	55	60	70	80	180
$\mu(D)$	3·25	2·95	2·89	2·82	2·66	2·49	0
$X\ (\%)$	20·1	24·4	25·5	26·8	29·9	34·2	
$10^{12}{}_m K$	135·7	104·6	95·7	85·8	66·1	46·4	1·3
$X\ (\%)$	15·6	20·3	22·2	24·8	32·3	46·4	

1,2-Dibromopropane

$\theta\ (°)$	0	50	60	65	70	80	180
$\mu(D)$	3·48	3·15	3·01	2·93	2·85	2·67	0
$X\ (\%)$	9·3	11·3	12·4	13·1	13·9	15·9	
$10^{12}{}_m K$	277·9	184·6	147·9	129·1	110·4	75·1	3·1
$X\ (\%)$	4·5	6·8	8·5	9·8	11·5	17·1	

1-Chloro-2-cyanoethane

$\theta\ (°)$	0	50	60	65	70	80	180
$\mu(D)$	5·10	4·68	4·59	4·49	4·39	3·29	1·66
$X\ (\%)$	34·7	42·2	44·1	46·2	48·7	51·7	
$10^{12}{}_m K$	601·9	374·8	300·9	264·5	229·9	168·7	92·7
$X\ (\%)$	16·1	29·0	39·3	47·6	59·6	107·6	

1-Bromo-2-cyanoethane

$\theta\ (°)$	0	60	65	70	75	80	180
$\mu(D)$	5·22	4·59	4·48	4·37	4·25	16·97	2·37
$X\ (\%)$	30·7	40·9	43·2	45·7	48·8	52·3	
$10^{12}{}_m K$	720·8	327·7	280·5	234·7	193·2	154·6	94·0
$X\ (\%)$	10·6	28·4	35·6	47·2	66·9	109·4	

Using $b_L{}^{C-CN} = 0·380,\ b_T{}^{C-CN} = b_V{}^{C-CN} = 0·165.$

1-Chloro-2-cyanoethane

$\theta\ (°)$	0	50	55	60	65	70	180
$\mu(D)$	5·10	4·68	4·59	4·49	4·39	4·29	1·66
$X\ (\%)$	34·7	42·2	44·1	46·2	48·7	51·7	
$10^{12}{}_m K$	540·1	328·5	294·3	260·0	226·0	194·3	84·2
$X\ (\%)$	19·8	37·0	43·0	51·4	63·7	82·0	

1-Bromo-2-cyanoethane

$\theta\ (°)$	0	50	60	65	70	80	180
$\mu(D)$	5·22	4·78	4·59	4·48	4·37	16·97	2·37
$X\ (\%)$	30·7	37·4	40·9	43·2	45·7	52·3	
$10^{12}{}_m K$	659·5	377·3	285·4	242·4	200·4	125·3	87·4
$X\ (\%)$	12·8	25·2	36·9	47·1	64·6		

Using $b_L{}^{C-CN} = 0·360,\ b_T{}^{C-CN} = b_V{}^{C-CN} = 0·165.$

2,3-Dibromo-2,3-dimethylbutane

$\theta\ (°)$	0	50	60	65	70	75	80	180
$\mu(D)$	4·14	3·75	3·59	3·49	3·39	3·29	3·17	0
$X\ (\%)$	4·3	5·2	5·7	6·1	6·4	6·8	7·3	
$10^{12}{}_m K$	900·8	543·4	430·0	366·6	310·5	255·4	204·6	14·3
$X\ (\%)$	1·6	2·7	3·5	4·1	4·9	6·0	7·6	

1,2-Dichloro-2-methylpropane

$\theta\ (°)$	0	50	55	60	65	70	180
$\mu(D)$	4·24	3·84	3·76	3·67	3·58	3·47	1·96
$X\ (\%)$	13·2	16·1	16·8	17·6	18·5	19·7	
$10^{12}{}_m K$	373·1	217·4	197·0	167·5	143·2	118·5	3·1
$X\ (\%)$	6·7	11·6	12·8	15·1	17·7	21·5	

TABLE 2 (Continued)

2,3-Dichloropropene

	(cis)						(trans)
$\theta\ (°)$	0	50	55	60	65	70	180
$\mu(D)$	3·22	2·94	2·88	2·81	2·74	2·67	0·73
$X\ (\%)$	21·2	25·9	27·0	28·3	29·9	31·6	
$10^{12}{}_m K$	276·5	127·9	104·0	80·6	58·2	36·0	17·4
$X\ (\%)$	7·19	16·87	21·52	29·49	45·69	100·00	

Using $b_L{}^{C-Cl} = 0·320,\ b_T{}^{C-Cl} = b_V{}^{C-Cl} = 0·220.$

$\theta\ (°)$	0	60	70	75	77	79	80	180
$\mu(D)$	3·22	2·81	2·67	2·59	2·56	2·53	2·51	0·73
$X\ (\%)$	21·2	28·3	31·6	33·7	34·7	35·7	36·2	
$10^{12}{}_m K$	470·6	165·4	82·9	65·9	53·1	41·6	36·5	33·0
$X\ (\%)$	0·7	2·3	6·1	9·2	15·1	35·1	85·9	

Using $b_L{}^{C-Cl} = 0·399,\ b_T{}^{C-Cl} = b_V{}^{C-Cl} = 0·185.$

$\theta\ (°)$	0	50	60	65	70	75	180
$\mu(D)$	3·22	2·94	2·81	2·74	2·67	2·59	0·73
$X\ (\%)$	21·2	25·9	28·3	29·9	31·6	33·7	
$10^{12}{}_m K$	359·5	164·1	102·4	78·4	45·2	27·6	23·8
$X\ (\%)$	3·7	8·7	15·6	22·5	57·1	323·8	

Using $b_L{}^{C-Cl} = 0·399,\ b_T{}^{C-Cl} = b_V{}^{C-Cl} = 0·185$ and $b_L{}^{C-Cl} = 0·320,\ b_T{}^{C-Cl} = b_V{}^{C-Cl} = 0·220.$

[a] Percentage populations are defined by the equation
$$X = \frac{100 N_g}{N_g + N_t}$$
where N_t and N_g are the numbers of molecules having the *trans-* and *gauche*-conformations respectively.

The general procedure adopted here for the quantitative conformational analysis of the compounds under consideration consists of the determination of the two basic variables, the percentage of the *gauche*-form $(X\%)$
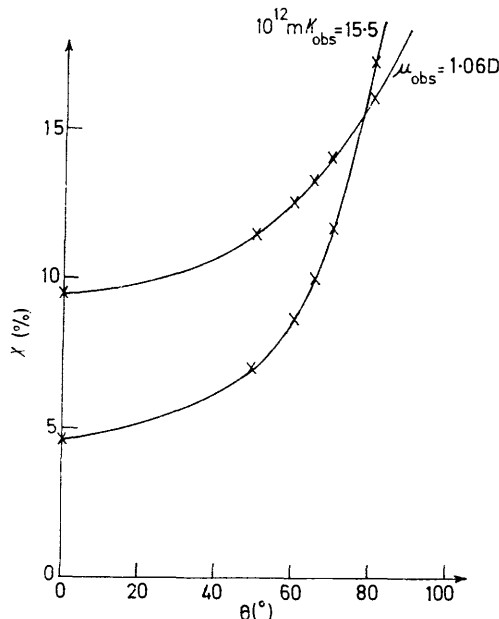
Variation of *gauche*-population (%) with dihedral angle (θ) calculated from experimental dipole moments and molar Kerr constants for 1,2-dibromopropane

and the dihedral angle (θ) for each of the substances examined. This can be done from our two experimental observations, the electric dipole moment which is a mean for the mixture of rotamers, and the molar Kerr constant which is likewise an average value. Given a value for the mean dipole moment, it is possible on certain assumptions [12b] to calculate X as a function of

θ; and it is also possible to do this given a value of the molar Kerr constant. Thus provided that the curves of X against θ from moment and from Kerr constant have different shapes, it is possible by superimposing them and finding where they intersect to obtain agreement as to the values of θ and $X\%$. A typical set of curves for 1,2-dibromopropane is shown in Figure 1. The required bond and group polarisability values are in Table 3. In

TABLE 3
Bond polarisability values (in units of 10^{-23} cm³)

Bond	b_L	b_T	b_V	Ref.
C–H	0·064	0·064	0·064	13
C–C	0·099	0·027	0·027	13
C–Cl	0·356	0·200	0·200	14
	0·320	0·220	0·220	13
	0·390	0·160	0·160	13
	0·399	0·185	0·185	15
C–Br	0·534	0·272	0·272	14
	0·460	0·310	0·310	13
C–CN	0·380	0·165	0·165	16
	0·360	0·175	0·175	16
C=C	0·280	0·073	0·077	17

the calculation of the molar Kerr constants of the various conformations, the cartesian axes to which the bond or group moments and polarisabilities are resolved are the x-axis along the central C–C bond, the z-axis perpendicular to one of the C–C–A planes (where A is the polar group), and the y-axis perpendicular to both these axes but lying in the plane containing C–C–A. In the case of 2,3-dichloropropene, A refers to the chlorine atom attached to the sp^3 hybridised carbon atom.

2,3-Dichloro- and 2,3-Dibromo-butanes.—Physical studies on the 2,3-dihalogenobutanes by electron diffraction measurements,[18] i.r.,[19,20] Raman,[21] and n.m.r. spectroscopy [22,23] have established the existence of three rotational isomers each for the *meso*-(I)—(III) as well as the racemic (IV)—(VI) diastereoisomers, (II) being the mirror image of (III). The relative stabilities of the rotational isomers of the compounds in the various states as determined by other workers are summarised in Table 4.

The general trends in relative energies for the *meso*-isomers of the vapours have been further shown to be consistent with theoretical values.[24] However the calculated and observed energy differences for the isomers of the (±)-compounds only agree if the observed values are reversed in sign, *i.e.* the calculated order of stability in the gas phase is $S_{HX} > S_{HH} > S_{CH_3}$ for both (±)-dichlorobutane and (±)-dibromobutane. This discrepancy has been attributed to a questionable assignment [20] of the vibrational energy transitions, arising from a lack of distinguishing elements of symmetry

between the isomers. Our dipole moment results may be considered in the light of this information. Three points of interest emerge from Table 1. (i) The moment of *meso*-2,3-dichlorobutane (1·63 D) is greater than that
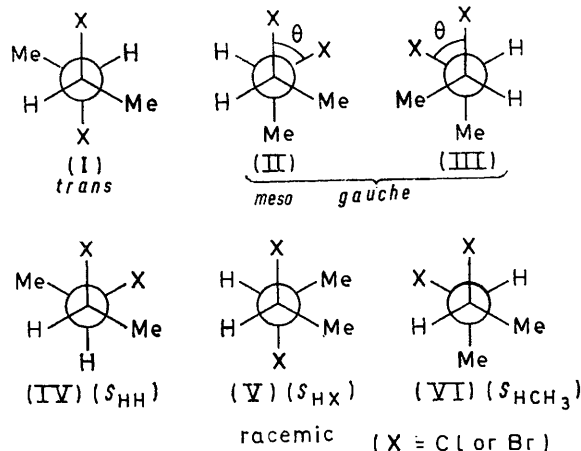
of *meso*-2,3-dibromobutane (1·41 D); (ii) the moment of racemic 2,3-dichlorobutane (1·79 D) is greater than that of racemic 2,3-dibromobutane (1·32 D); and (iii) although the moment of racemic 2,3-dichlorobutane is

TABLE 4
Relative stabilities of rotational isomers of *meso*- and (±)-2,3-dichloro- and -2,3-dibromo-butanes

Molecule	State	Relative stability of rotational isomer	Method	Ref.
meso-2,3-Di-chlorobutane	Vapour	*trans* > *gauche*	I.r.	19, 20
	Liquid	*trans* > *gauche*	I.r.	20
	Solution	*trans* > *gauche*	I.r.	20
			N.m.r.	22, 23
meso-2,3-Di-bromo-butane	Vapour	*trans* > *gauche*	I.r.	20
	Liquid	*gauche* > *trans*	I.r.	20
		trans > *gauche*	I.r.	19
	Solution	*trans* > *gauche*	I.r.	19, 20
			N.m.r.	22, 23
(±)-2,3-Di-chlorobutane	Vapour	$S_{HCH_3} > S_{HH} \approx S_{HX}$	I.r.	20
	Liquid	$S_{HX} \approx S_{HH} > S_{HCH_3}$	I.r.	20
	Solution	$S_{HX} \approx S_{HH} \approx S_{HCH_3}$	N.m.r.	22
(±)-2,3-Di-bromobutane	Vapour	$S_{HCH} > S_{HH} \approx S_{HX}$	I.r.	20
	Liquid	$S_{HH} > S_{HCH_3} > S_{HX}$	I.r.	20
		$S_{HX} > S_{HH} \approx S_{HCH_3}$	I.r.	19
	Solution	$S_{HX} > S_{HH} \approx S_{HCH_3}$	I.r.	19
			N.m.r.	22

higher than that of the *meso*-form the order is reversed in the case of *meso*- and racemic 2,3-dibromobutane.

Points (i) and (ii) can be simply explained by postulating relative increases in the concentrations of the non-polar rotamers (I) and (V) in the equilibria (I) ⇌ (II) ⇌ (III) and (IV) ⇌ (V) ⇌ (VI) respectively,

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when chlorine is replaced by the bulkier bromine. The polarities of the C–Cl and C–Br bonds need not be considered because they are virtually the same.

In the case of point (iii) the relative order of moments in the diastereoisomers of 2,3-dichlorobutane may be attributed to a higher concentration of (I) in the meso-than of (V) in the racemic rotameric mixture. This is because in (I), all the polar (Cl–Cl) and steric (Cl–Cl and Me–Me) interactions are minimised whereas the Me–Me steric repulsions would result in the destabilisation of (V). When we consider 2,3-dibromobutane, substitution of chlorine by bromine would result in stronger halogen–halogen (repulsive) interactions. Since halogen–Me interactions are attractive,[25] these would reduce the moments of (IV) and (VI) by a widening of the dihedral angle between the polar bonds, more than in the case of (II) and (III) with the result that the moment of meso-2,3-dibromobutane now exceeds that of racemic 2,3-dibromobutane.

Table 5 shows that the dihedral angle in meso-2,3-dibromobutane (81°) is wider than that in the chloro-analogue (76°). Here again, the greater volume of the

TABLE 5

Summary of the percentage of gauche- and trans-conformers, ΔE and θ

| Compound	gauche (%)	trans (%)	$\Delta E/$ kcal mol^{-1} [a]	θ (°)
meso-2,3-Dichloro-butane	41	59	0·627	76
meso-2,3-Dibromo-butane	27	73	1·001	81
1,2-Dichloropropane	28	72	0·971	65
1,2-Dibromopropane	15	85	1·439	77
1-Chloro-2-cyano-ethane	49	51	0·434	66 [b]
	45	55	0·530	56 [b]
1-Bromo-2-cyano-ethane	45	55	0·530	69 [b]
	42	58	0·602	63 [b]
2,3-Dibromo-2,3-dimethylbutane	7	93	1·944	79
1,2-Dichloro-2-methylpropane	19	81	1·270	67
2,3-Dichloropropene	28	72	0·971	59 [c]
	36	64	0·752	79 [c]
	31	69	0·885	68 [c]

[a] The energy difference ΔE is calculated from the equation $N_g/N_t = 2e^{-\Delta E/RT}$, assuming that the various conformations are equal in entropy. [b] Calculations based on C≡N bond polarisability values for propionitrile and acetonitrile respectively. [c] Calculations based on C–Cl bond polarisability values for methyl chloride, vinyl chloride, and a combination of both methyl chloride and vinyl chloride

bromine atom in determining steric consequences is very much in evidence.

The percentage populations of the gauche- and trans-isomers obtained in this work for meso-2,3-dichloro-butane (gauche, 41; trans, 59%) and meso-2,3-dibromo-butane (gauche, 28; trans, 72%) are in reasonable agreement with those obtained from n.m.r. studies:[22] meso-2,3-dichlorobutane (gauche, 48; trans, 52%); meso-

2,3-dibromobutane (gauche, 30; trans, 70%). Agreement with i.r. estimates [19,26] however, is less satisfactory: meso-2,3-dichlorobutane (gauche, 28; trans, 72%), meso-2,3-dibromobutane (gauche, 22; trans, 78%). An approximate estimate of the population distribution in the (±)-compounds may be obtained if we assume that the dipole moments of the rotamers (IV) and (VI) are the same. For dihedral angle values of 76 and 81° respectively for (±)-2,3-dichlorobutane and (±)-2,3-dibromobutane, the estimates are 51% trans for the chloro- and 75% trans for the bromo-compound. These results are in qualitative agreement with the relative order deduced theoretically [24] and with other conclusions drawn from our dipole moment data.

1,2-Dihalogenopropanes.—The i.r. spectra [27] of 1,2-dichloropropane and 1,2-dibromopropane have been interpreted in terms of the three rotational isomers, trans, gauche, and gauche'. The trans-form alone was observed in the solid but in the liquid state both trans and gauche-forms are believed to be present. In the gaseous state, the trans-form is the predominant species although with rising temperature, the population of the gauche- and gauche'-rotamers increases at the expense of the trans. The evidence for the existence of the three rotational isomers appears to receive further support from ultrasonic relaxation measurements.[28] On the other hand, Finegold [29] concluded from his n.m.r. study of the 1,2-dihalogenopropanes that the concentration of the gauche' form in the equilibrium mixture is negligible, pointing out that Thomas and Gwinn [30] had come to the same conclusion in the case of 1,1,2-tri-chloroethane where the steric situation is analogous.

trans   gauche   gauche'

(X = Cl or Br)
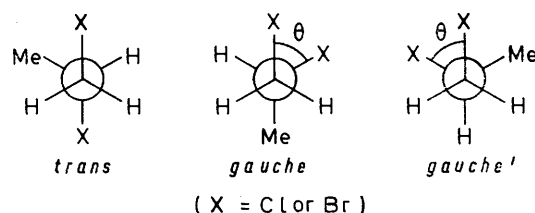
In our calculations of dipole moment and Kerr constants, the assumption has been made that both gauche- and gauche'-rotamers have the same dihedral angle θ and dipole moment. Table 5 shows that the values of the dihedral angle and the combined percentage populations of the gauche- and gauche'-rotamers obtained in this work are 65° and 28% for 1,2-dichloro-propane and 77° and 15% for 1,2-dibromopropane (Altona and Hageman [9a] obtain 88% for the trans-rotamer of 1,2-dibromopropane from its dipole moment of 1·13 D for carbon tetrachloride solution.) The fact that the dipole moment of 1,2-dichloropropane (1·46 D) is higher than that of 1,2-dibromopropane (1·06 D) may be attributed to the larger steric effects of bromine. Furthermore, the smaller dihedral angle of

[25] N. Sheppard, Adv. Spectroscopy, 1959, 1, 288.
[26] K. Iimura, N. Kawakami, and M. Takeda, Bull. Chem. Soc. Japan, 1969, 42, 2091.
[27] Riyoshi-Nakamura, Nippon Kagaku Zasshi, 1957, 78, 1158.

[28] R. A. Padmanaban, J. Sci. Ind. Res., 1960, 19B, 457.
[29] H. Finegold, J. Chem. Phys., 1964, 41, 1808.
[30] J. R. Thomas and W. D. Gwinn, J. Amer. Chem. Soc., 1949, 71, 2785.

65° in 1,2-dichloropropane would enhance its overall moment, when compared with 1,2-dibromopropane (77°).

1-*Cyano-2-halogenoethanes*.— 1-Cyano-2-halogeno-ethanes belong to the class of ethanes which can be described by the general formula XCH_2CH_2Y (X = Cl or Br, Y = CN in this context). Two sets of values for the

CN   CN   CN

trans   gauche

(X = Cl or Br)
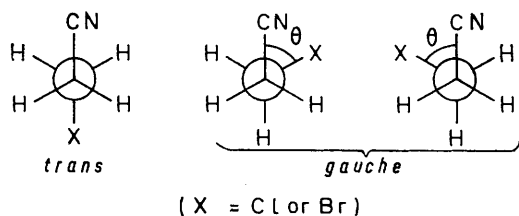
bond polarisability for the cyano-group [16] were used in the calculation of molar Kerr constants for the various conformations of each 1-cyano-2-halogenoethane: those derived from propionitrile ($b_L{}^{C-CN} = 0.380$, $b_T{}^{C-CN} = b_V{}^{C-CN} = 0.165$), and those from acetonitrile ($b_L{}^{C-CN} = 0.360$, $b_T{}^{C-CN} = b_V{}^{C-CN} = 0.175$). Thus two sets of results are obtained for the dihedral angle and percentage *gauche*-population: 1-chloro-2-cyanoethane, 49% (44%), θ = 66° (56°); 1-bromo-2-cyanoethane, 45% (42%), θ = 69° (63°). The results in parentheses are obtained with C–CN bond polarisability values drawn from acetonitrile.

The larger dipole moment of 1-chloro-2-cyanoethane (3·29 D) compared with that of 1-bromo-2-cyanoethane (3·16 D) may be a partial reflection of the smaller value of the dihedral angle in the former compound. Our results also show that in carbon tetrachloride the rotamer distribution is almost equimolecular for both compounds, with the balance somewhat in favour of the *trans*-rotamer, in agreement with the n.m.r. study of 1-bromo-2-cyanoethane by Deb and Abraham.[31] By contrast, spectroscopic studies [32] have shown that the *gauche*-rotamer is the more stable species in the liquid and further, both 1-chloro-2-cyanoethane and 1-bromo-2-cyanoethane exist in the *gauche*-conformation in the solid state.

The values of the dihedral angles in these compounds need some comment since on the grounds of steric and dipole–dipole interactions, one might expect them to lie between those for succinonitrile (90°) and the 1,2-dichloro- and 1,2-dibromo-ethanes (*ca.* 70°). In point of fact, they turn out to be lower than the values of all these molecules (Table 5). One possible way of explaining these unexpectedly low values, is to postulate that the large C≡N dipole induces a moment in the polarisable halogen atom which is thus attracted to the C≡N group.

2,3-*Dibromo-2,3-dimethylbutane*.—From Table 5 it is seen that the observed dipole moment (0·96 D) and

molar Kerr constant ($10^{12}\,_mK = 29$) for carbon tetra-chloride solution are compatible with a mixture containing 7% of the *gauche*-rotamer with a dihedral angle of 79°. Spectroscopic,[33] acoustic absorption,[33] and dipole moment [10] studies have been carried out on 2,3-dibromo-2,3-dimethylbutane. Our result that only *ca.* 7% of the *gauche*-rotamer is present in carbon tetrachloride solution is in good agreement with the 6% found by Altona and Hageman [9a] from dipole moment measurements. The additional parameter we have determined, namely the value of the dihedral angle (79°), indicates that there are strong steric repulsive forces between the bromine atoms resulting in the destabilisation of the *gauche*-rotamer.

1,2-*Dichloro-2-methylpropane*.—The infrared and Raman spectra [34-36] of 1,2-dichloro-2-methylpropane have shown that the molecules exist as equilibrium mixtures of *gauche-* and *trans*-rotamers in the gaseous and liquid states, but only in the *trans*-form in the solid

Cl   Cl   Cl
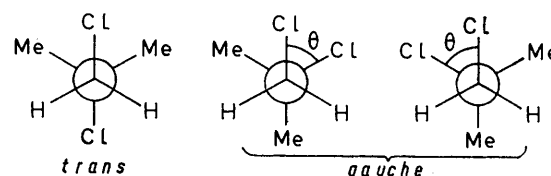
trans   gauche

state. From the relative intensities of the i.r. and Raman bands [9b] associated with the *gauche-* and *trans*-rotamers, Altona and Hageman concluded that the *trans* is the more stable species in solution. Our calculations show that indeed the *trans*-rotamer occurs in solution to the extent of 81%. Moreover the dihedral angle is now found to be 67° for the *gauche*-rotamer. The fact that this value is lower than that characterising 1,2-dichloro-ethane appears to be related to non-bonded Cl–Me interactions.

2,3-*Dichloropropene*.—From the variation of long range coupling constants with solvents in the n.m.r. spectra of 2,3-dichloropropene, Whipple *et al.*[37] inferred the

Cl CH₂   Cl   Cl
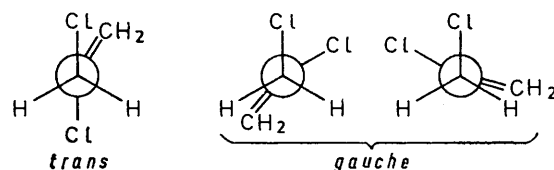
trans   gauche

existence of *trans-* and *gauche*-rotamers in rapid equilibrium. This view is consistent with the Raman [38] and i.r. spectra [39] of the compound. The relative stabilities of the rotational isomers will depend on the energies of the *trans-* and the *gauche*-conformers as derived from the algebraic sum of the steric and polar interactions between the non-bonded substituents. Dipole moment evi-

[31] K. K. Deb and R. J. Abraham, *J. Mol. Spectroscopy*, 1967, **23**, 393.

[32] E. Wyn-Jones and P. W. J. Orville-Thomas, *J. Chem. Soc.* (*A*), 1966, 101.

[33] E. Wyn-Jones and P. J. D. Park, *J. Chem. Soc.* (*A*), 1968, 2064.

[34] M. Hayashi, I. Ichishima, T. Shimanouchi, and S. Mizu-shima, *Spectrochim. Acta*, 1957, **10**, 1.

[35] M. Hayashi, *Nippon Kagaku Zasshi*, 1951, **78**, 536.

[36] K. W. F. Kohlrausch and L. Kahovec, *Z. phys. Chem.* (*Frankfurt*), 1940, **48b**, 7.

[37] E. B. Whipple, J. H. Goldstein, and G. R. McClure, *J. Amer. Chem. Soc.*, 1960, **82**, 3811.

[38] A. Kirrman, *Bull. Soc. chim. France*, 1948, 170.

[39] G. A. Crowder, (*a*) *J. Mol. Spectroscopy*, 1966, **20**, 430; (*b*) 1967, **23**, 103.

dence [12a] has already indicated that the *trans*-rotamer is more stable than the *gauche* by 0·914 kcal mol⁻¹. Our results (θ = 59, 79, and 68°; % *gauche* 28, 36, and 31) confirm this order of relative stability.

In our calculations, the dipole moments for different values of the dihedral angle (θ) of 2,3-dichloropropene are computed from equation (1) where $A = \mu_1^2 + \mu_2^2 -$

$$\mu^2(\theta) = A + B\cos\theta \qquad (1)$$

$2\mu_1\mu_2 \cos\phi_1 \cos\phi_2$ and $B = 2\mu_1\mu_2 \sin\phi_1 \sin\phi_2$, μ_1 and μ_2 being the group moments of the two different polar substituents taken as 1·72 (methyl chloride) and 1·44 D (vinyl chloride), and ϕ_1 and ϕ_2 the angles between the two polar groups and the C–C bond (110° for =C–C–Cl and 120° for C=C–Cl respectively [14]). Three sets of bond polarisabilities for the C–Cl bond were used for the Kerr constant calculations, drawn from methyl chloride, vinyl chloride, and a combination of these for the sp^3 and sp^2 bonded halogen atoms of 2,3-dichloropropene.

The molar Kerr constant of an analogous compound, 3-chloropropene, has been measured [14] and the dihedral

⁴⁰ H. J. M. Bowen, A. Gilchrist, and L. E. Sutton, *Trans. Faraday Soc.*, 1955, **51**, 1341.

angle between the methylene group (C=CH₂) and the C–Cl bond was found to be 120° (see Figure). This
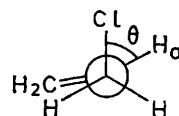
finding is reconcilable with the non-planar conformation specified by Bowen *et al.* in an electron diffraction study.⁴⁰ A comparison (based on steric considerations) between 2,3-dichloropropene and 3-chloropropene suggests that the dihedral angle θ in the former should be somewhat larger than that in the latter compound. In 3-chloropropene, the angle between C–Cl and $CH_a(\theta)$ is 60°. The dihedral angle between the two C–Cl bonds in 2,3-dichloropropene is 59, 68, or 79° depending on the polarisability values used in our calculations. From the standpoint of balancing steric interactions, the result 68° appears to be the most reasonable value; moreover it has the merit that it is based on the most realistic choice of polarisability parameters. Thus we conclude that the dihedral angle in 2,3-dichloropropene is likely to be *ca.* 68°.