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CONFORMATION OF NON-AROMATIC RING COMPOUNDS—XLVII[1]

THE CONFORMATION OF *trans*-1,2-DIHALOGENOINDANS

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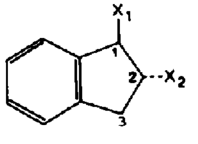
Abstract—Dipole moments, NMR, IR and Raman spectra of *trans*-1,2-dihalogenoindans were determined. Linear relations were found to exist between the squares of the dipole moments and the vicinal proton spin coupling constants. It is concluded that the diaxial conformer predominates in solution.

INTRODUCTION

IN CONTINUATION of our studies on the conformation of halogenated 5-membered alicyclic[2-7] and heterocyclic[8] ring compounds, the present paper investigates the conformational properties of the *trans*-1,2-dihalogenoindans, where a cyclopentene ring is fused to a benzene ring.* The following compounds were studied by means of dipole moments, NMR, IR and Raman spectroscopy: *trans*-1,2-dichloro- (I), *trans*-2-bromo-1-chloro- (II) and *trans*-1,2-dibromoindan (III).



I: $X_1 = X_2 = Cl$
II: $X_1 = Cl, X_2 = Br$
III: $X_1 = X_2 = Br$

FIG. 1.

The conformation of the cyclopentene ring. The conformation of the cyclopentene ring is assumed to be that of an envelope, because the torsional forces about a double bond are so much larger than those about single bonds as to cause planarity of four of the five C atoms[14] (atoms 1, 2, 3 and 5 in Fig. 2).

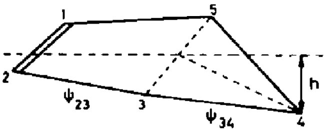


FIG. 2 Cyclopentene model

Planar cyclopentene contains two eclipsed ethane fragments and two staggered propene fragments. When the molecule is puckered there is a decrease in eclipsing

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* Whereas the halogenoindanones have been quite thoroughly studied by means of dipole moments[9] and spectroscopic methods,[10-13] no studies on the conformation of halogenoindans have thus far appeared in the literature.

energy along two bonds and a smaller increase in eclipsing energy along the other bonds. Therefore, the total eclipsing energy decrease as the molecule is puckered is smaller than in cyclopentane. The planar constellation represents a barrier separating two energy minima (Fig. 3), which may have different conformational properties (e.g. with axial and equatorial substituents).

The detailed equilibrium conformation of cyclopentene has been calculated by minimizing the bond angle strain and torsional strain.[14–16] The largest ring dihedral angle ψ_{34} was found to be 20–25°, in good agreement with the results from microwave investigations.[17,18] The relation between the out-of-plane distance of C-4 (h) and the dihedral angles ψ_{23} and ψ_{34} was calculated by James.[15]

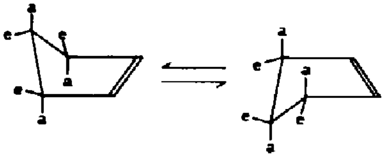

FIG. 3 The conformers of cyclopentene with axial and equatorial valencies.

RESULTS

A. *Dipole moments and NMR spectra*

The dipole moments at 25° and the 100 Mc/s NMR spectra of compounds I–III were measured in benzene and in carbon tetrachloride.* Consider the following system (Fig. 4):

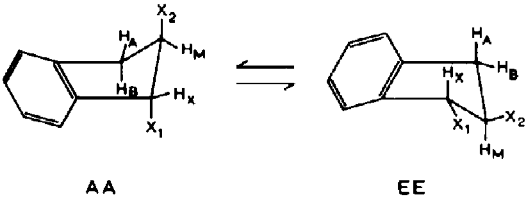

FIG. 4 The conformers of *trans*-1,2-dihalogenoindans.

As the differences in the chemical shifts of the individual protons are large compared with their coupling constants, the derivation of these parameters from the spectra was based on the ABMX approximation,[20] with $J_{AX} = J_{BX} = 0$. In order to test the validity of this approximation, the parameters found were used to calculate exact ABCD spectra.† These spectra were subsequently analyzed as ABMX spectra, yielding coupling constants that were practically equal (within 0·1 c/s) to the input values.

The hydrogen at C-1 (H_X) appears at the lowest field, followed in turn at higher fields by the hydrogen at C-2 (H_M) and the two hydrogens at C-3 (H_A and H_B). The H_X signal appears as a doublet having the separation J_{MX}. The H_M resonance is rather complex; the distance between the outer peaks is equal to $J_{AM} + J_{BM} + J_{MX}$.

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* The 60 Mc/s NMR spectrum of compound III in $CDCl_3$ has been reported.[19]

† The calculations were carried out on an X1 computer by means of a Frequint IV program.

H_A and H_B yield an octet (AB of an ABMX type, in which X has only a minimal influence on AB). The peaks at the higher field were assigned to H_A, because J_{MX} is expected to be closer in value to J_{AM} than to J_{BM} (the dihedral angle ψ_{AM} is equal to ψ_{MX}; the small difference between J_{AM} and J_{MX} is due to an electronegativity effect, see below).

The values of the chemical shifts, coupling constants and dipole moments of compounds I–III are presented in Table 1. The sign of the geminal coupling constant J_{AB} is supposed to be negative on account of data for similar ring systems.[21,22]

The observed values of μ^2 are related to μ^2_{AA} and μ^2_{EE} of the individual diaxial and diequatorial conformers by:

$$\mu^2 = x_{AA}\mu^2_{AA} + (1 - x_{AA})\,\mu^2_{EE} \tag{1}$$

where x_{AA} is the molar fraction of the diaxial form ($x_{AA} + x_{EE} = 1$). Similarly, the vicinal coupling constants are related by the expression:

$$J = x_{AA}J_{AA} + (1 - x_{AA})\,J_{EE} \tag{2}$$

From Eqs (1) and (2) it is seen that a linear relation between μ^2 and J should exist[3,5,6,23] with a slope:

$$H = \mathrm{d}\mu^2/\mathrm{d}J = (\mu^2_{EE} - \mu^2_{AA})/(J_{EE} - J_{AA}) \tag{3}$$

Figure 5 shows plots of μ^2 against J_{AM} and J_{MX}, which obey the relations:

$$\mu^2 = 0{\cdot}62J_{AM} + 1{\cdot}65 \tag{4}$$

$$\mu^2 = 0{\cdot}73\,J_{MX} + 1{\cdot}64 \tag{5}$$

TABLE 1. DIPOLE MOMENTS (D), CHEMICAL SHIFTS (PPM FROM TMS) AND COUPLING CONSTANTS (c/s) FOR *trans*-1,2-DIHALOGENOINDANS IN BENZENE (B) AND IN CARBON TETRACHLORIDE (T)

Compound	Dichloro- (I)		Bromochloro- (II)		Dibromo- (III)	
Solvent	B	T	B	T	B	T
μ	2·01	1·95	1·89	1·84	1·54	1·55
δH_A	2·80	2·97	2·92	3·11	2·94	3·09
δH_B	3·25	3·47	3·36	3·60	3·43	3·60
δH_M	4·32	4·43	4·37	4·49	4·63	4·74
δH_X	5·09	5·16	5·25	5·32	5·50	5·57
J_{AB}	−16·9	−16·9	−17·2	−17·0	−17·5	−17·7
J_{AM}	3·9	3·5	3·1	2·8	1·2	1·2
J_{BM}	6·0	6·0	5·8	5·8	5·3	5·3
J_{MX}	3·2	3·0	2·7	2·5	1·0	1·0

It is supposed that the dibromo compound III exists almost exclusively in the diaxial conformation for the following reasons:

(i) An allylic Br atom prefers to occupy exclusively the axial position in the cyclohexene system.[24–26]

(ii) No increase of the dipole moment and vicinal coupling constants of the dibromo compound on changing the solvent from carbon tetrachloride to benzene is observed, whereas a small increase of these parameters occurs for the dichloro and bromo-chloro compounds I and II. This suggests that the equilibrium in the dibromo derivative lies far towards one (i.e. the diaxial) conformer.

(iii) In the diaxial conformer, the torsional angles between the equatorial protons, ψ_{AM} and ψ_{MX}, are of the order of 95°. Therefore, on account of the *Karplus**[27] equation:

$$J_{HH} = A\cos^2\psi_{HH} - B\cos\psi_{HH} + C \qquad (6)$$

J_{AM} and J_{MX} should have a low value of about 0·5–1·5 c/s, which is in good agreement with the observed coupling constants of *trans*-1,2-dibromoindan.

(iv) The IR spectra of compound III in the liquid (solution in CS_2) and solid (KBr pellet) state are identical (cf. section B), suggesting that only one conformer is present in solution.

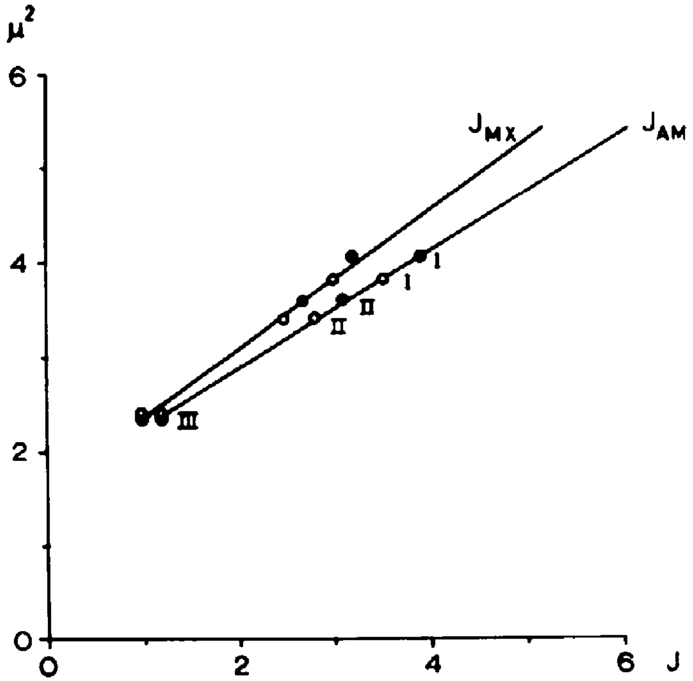

FIG. 5 μ^2 against J_{AM} and J_{MX} for compounds I–III. ● Solutions in benzene, ○ solutions in carbon tetrachloride.

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* The theoretical *Karplus* parameters (for ethane) are: $A = 9$, $B = 0{\cdot}5$, $C = -0{\cdot}3$ c/s. However, different systems require different parameters. Throughout this paper an arbitrary value of $B = 0{\cdot}5$ c/s will be retained (cf. Ref. 5).

Therefore, we assume for the *trans*-1,2-dihalogenoindans: $\mu_{AA} = 1{\cdot}5\ D$. The dipole moment of the diequatorial conformer can be calculated with the aid of Eqs (7) and (8), derived in Ref. 5:

$$\mu_{AA}^2 = 4\mu_p^2 \sin^2\alpha \cos^2 \tfrac{1}{2}(120 + \psi) + D \tag{7}$$

$$\mu_{EE}^2 = 4\mu_p^2 \sin^2\alpha \cos^2 \tfrac{1}{2}(120 - \psi) + D \tag{8}$$

where μ_p is the partial moment along the C—X bond, α is the valency angle C—C—X and ψ is the ring dihedral angle. The correction term D accounts for the induced moment in the ring. Taking $\mu_{AA} = 1{\cdot}5\ D$, $\mu_p = 2{\cdot}05\ D^{28}$, $\alpha = 110{\cdot}5°$, $\psi = 25°$[*], it follows that the induction term $D = 0{\cdot}91\ D^2$, yielding a value of $2{\cdot}7_5\ D$ for μ_{EE}.

The relation between the experimental slope $H = \mathrm{d}\mu^2/\mathrm{d}J$ and the Karplus parameters A and B was also derived in Ref. 5:

$$H = \mathrm{d}\mu^2/\mathrm{d}J = \frac{2\mu_p^2 \sin^2\alpha}{A\cos\psi + B} \tag{9}$$

Introducing the following set of parameters into expressions (4), (5), (6) and (9): $H_1 = \mathrm{d}\mu^2/\mathrm{d}J_{\mathrm{AM}} = 0{\cdot}62$, $H_2 = \mathrm{d}\mu^2/\mathrm{d}J_{\mathrm{MX}} = 0{\cdot}73$, $\psi = 25°$, $\mu_p = 2{\cdot}05\ D$, $\alpha = 110{\cdot}5°$, $\mu_{AA} = 1{\cdot}5\ D$, $\mu_{EE} = 2{\cdot}75\ D$, we find the following *Karplus* parameters and coupling constants for the —CHX—CH$_2$— moiety:

$$A = 12{\cdot}6,\ B = 0{\cdot}5,\ C = 0{\cdot}8\ \mathrm{c/s} \tag{10}$$

$$(J_{\mathrm{AM}})_{AA} = J_{2e3e} = 1{\cdot}0\ \mathrm{c/s} \tag{11}$$

$$(J_{\mathrm{AM}})_{EE} = J_{2a3a} = 9{\cdot}7\ \mathrm{c/s} \tag{12}$$

and for the —CHX—CHX— moiety:

$$A = 10{\cdot}6,\ B = 0{\cdot}5,\ C = 0{\cdot}7\ \mathrm{c/s} \tag{13}$$

$$(J_{\mathrm{MX}})_{AA} = J_{1e2e} = 0{\cdot}8\ \mathrm{c/s} \tag{14}$$

$$(J_{\mathrm{MX}})_{EE} = J_{1a2a} = 8{\cdot}2\ \mathrm{c/s} \tag{15}$$

The *Karplus* parameter A is greater for the —CHX—CH$_2$— than for the —CHX—CHX— moiety, in accord with the observation[27] that the vicinal coupling constants decrease with increasing electronegativity. The derivation of the *Karplus*

TABLE 2. MOLAR FRACTIONS x_{AA} AND FREE ENERGY DIFFERENCES ΔG°_{EE-AA} (kcal/mole) AT 25°C IN BENZENE AND IN CARBON TETRACHLORIDE

Compound	Benzene		Carbon tetrachloride	
	x_{AA}	ΔG°	x_{AA}	ΔG°
trans-1,2-dichloroindan	$0{\cdot}6_7$	$0{\cdot}4_2$	$0{\cdot}7_1$	$0{\cdot}5_4$
trans-2-bromo-1-chloroindan	$0{\cdot}7_6$	$0{\cdot}6_7$	$0{\cdot}7_9$	$0{\cdot}7_8$
trans-1,2-dibromoindan	$>0{\cdot}95$		$>0{\cdot}95$	

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[*] This value is chosen in accordance with the microwave data for cyclopentene.[17, 18]

parameters presented here is based on the assumption of trigonal symmetry about the projection axis and on the supposition that the orientation of a proton to the π-electron system of the benzene ring has no influence on its coupling constants.

With the aid of the experimental dipole moments and the values of μ^2_{AA} and μ^2_{EE} the molar fractions x_{AA} of compounds I and II were calculated. These values and the free energy differences at 25°, ΔG°_{EE-AA}, are collected in Table 2.

The following conclusions can be drawn from Table 2:

(i) The diaxial conformer is favoured over the diequatorial one. Down the series from chlorine to bromine an increase in percentage diaxial conformer is observed: this trend is similar in the *trans*-1,2-dihalogenocyclopentanes[3, 5] and in the *trans*-1,2-dihalogenocyclohexanes.[5, 29]

(ii) The "benzene effect", $\delta\Delta G^\circ = \Delta G^\circ$ (benzene)-ΔG° (CCl_4), is equal to 0·1 kcal/mole, i.e. much smaller than the values thus far observed for other vicinal *trans* dihalogenides (0·25–0·5 kcal/mole).[30] The "benzene effect" in vicinal dihalogenides may be mainly caused by the solvent-dependence of the halogen–halogen interaction in the diequatorial conformer;[30] the small value of $\delta\Delta G^\circ$ found for the dihalogenoindans might then be due to the large dihedral angle between the equatorial C–halogen bonds (95°), causing a small halogen–halogen interaction as compared with that in the cyclohexanes or cyclopentanes.

The X part of the NMR spectrum of the dichloro compound I was also taken in tetralin at several temperatures, ranging from 40–160°. The spectra show an increase of J_{MX} with temperature (Table 3).

TABLE 3. J_{MX} OF COMPOUND I IN TETRALIN AT SEVERAL TEMPERATURES

T (°C)	J_{MX} (c/s)
40	3·40
70	3·55
100	3·65
130	3·75
160	3·85

According to the relations $K = x_{EE}/(1 - x_{EE})$ and

$$\log K = -\frac{\Delta H^\circ}{2{\cdot}3RT} + \frac{\Delta S^\circ}{2{\cdot}3R} \tag{16}$$

a linear relation between log K and $1/T$ should exist (Fig. 6). The values of log K were calculated using the parameters $(J_{MX})_{AA} = 0{\cdot}8$ c/s and $(J_{MX})_{EE} = 8{\cdot}2$ c/s according to Eqs (14) and (15). From the plot of log K against $1/T$ we find:

$$\log K = -123/T + 0{\cdot}13 \tag{17}$$

It follows that: $\Delta H^\circ_{EE-AA} = 0{\cdot}5_7$ kcal/mole, $\Delta S^\circ_{EE-AA} = 0{\cdot}6$ e.u. Then ΔG°_{EE-AA} (25°) = 0·4 kcal/mole, in satisfactory agreement with the value calculated directly from J_{MX} at room temperature in tetralin (3·3 c/s gives ΔG°(25°) = 0·4 kcal/mole).

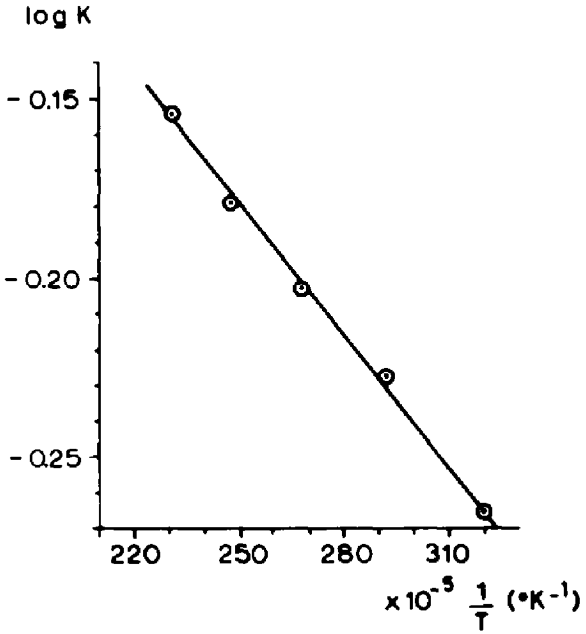

FIG. 6 Plot of log *K* against 1/*T* for *trans*-1,2-dichloroindan in tetralin.

B. *IR and Raman spectra*

The IR and Raman spectra between 400 and 800 cm^{-1} of the compounds I–III are presented in Table 5 (see also Figs 8 and 9). A comparison of the frequencies with the values of reported indan spectra[31, 32] shows a reasonable agreement.

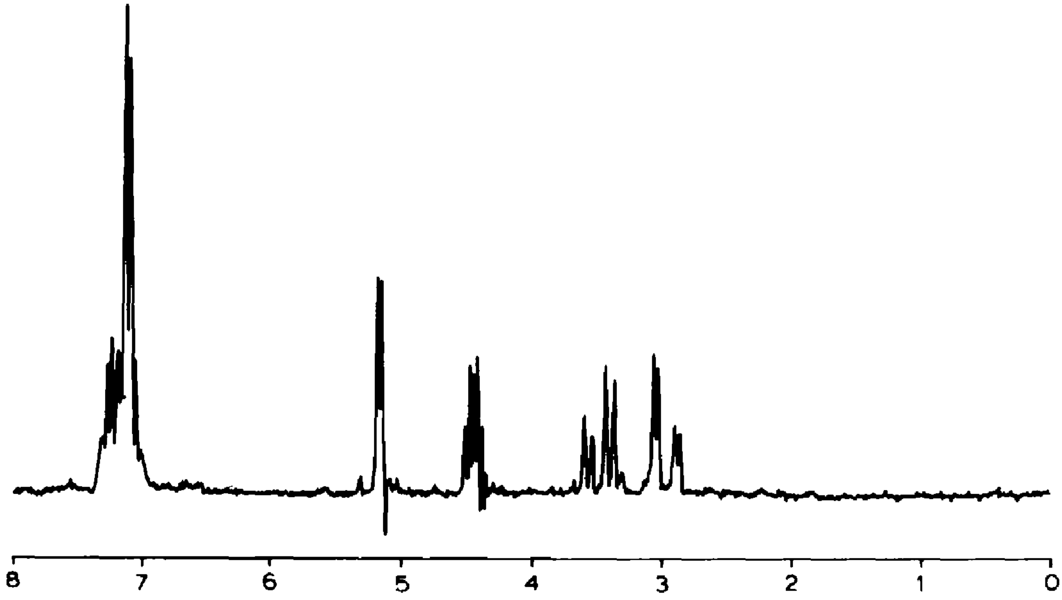

FIG. 7 100 Mc/s NMR spectrum of *trans*-1,2-dichloroindan in carbon tetrachloride.

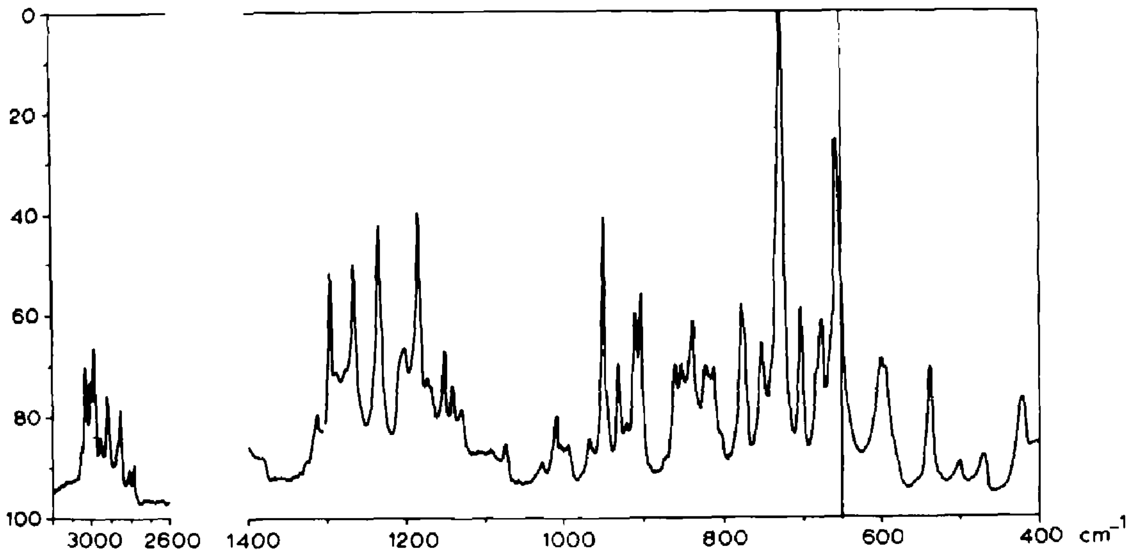

Fig. 8 IR spectrum of *trans*-1,2-dichloroindan (solution in CS_2).

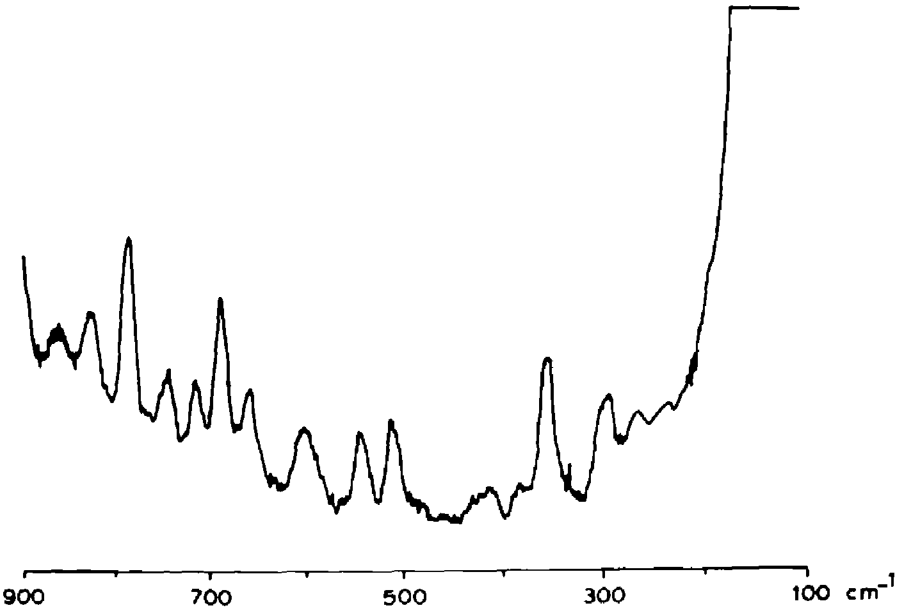

Fig. 9 Raman spectrum of *trans*-1,2-dichloroindan (solution in tetrahydrofuran).

In this region the C–halogen stretching vibrations should occur. These frequencies are highly dependent on the geometrical arrangement about the neighbouring C atoms. The single most important factor seems to be the nature (C, H, etc.) of the atom or atoms *anti* to the halogen. By an extension of a notation, introduced earlier,[33,34] was derived[35,36] an empirical set of parameters which allows the assignment of the C–Cl and C–Br stretching frequencies according to the chemical–geometrical combination (cf. also Ref. 37). The chemical type of halogenide is specified by P (primary), S (secondary) and T (tertiary), the atom or atoms in *anti*-position are indicated by a subscript (H, C, O, X (halogen), p (oxygen lone pair or π-electrons)). Various types of vibration are collected in Table 4. These values are probably accurate to ±20 cm^{-1}.

TABLE 4. C–Cl AND C–Br STRETCHING PARAMETERS FOR VARIOUS CHEMICAL–GEOMETRICAL COMBINATIONS

Type	C–Cl (cm^{-1})	C–Br (cm^{-1})
S_{HH}	611	535
S_{XH}	650	596
S_{CC}	742	686
S_{Hp}	561	537
S_{Xp}	708	632

TABLE 5. IR AND RAMAN SPECTRA OF *trans*-1,2-DIHALOGENOINDANS BETWEEN 400 AND 800 cm^{-1}

IR indan		Dichloro- (I)		Bromochloro- (II)		Dibromo- (III)	
Stanescu *et al.*[31]	Bardet *et al.*[32]	IR (CS_2)	Raman (THF)	IR (CS_2)	Raman (liq)	IR (CS_2)†	Raman (THF)
416 (s)	415	425 (w)	420 (20)	421 (w)	426 (11)	417 (w)	425 (w)
*	—	472 (vw)	480 (w)	464 (vw)	473 (9)	458 (vw)	467 (sh)
518 (m)	519	503 (vw)	514 (60)	501 (w)	510 (42)	486 (m)	493 (45)
584 (w)	584	540 (m)	545 (52)	535 (m)	540 (29)	530 (m)	534 (23)
616 (m)	615	600 (m)	600 (45)	586 (s)	589 (54)	593 (m)	594 (27)
—	—	662 (s)	658 (48)	605 (s)	606 (43)	572 (vs)	571 (27)
—	—	690 (m)	688 (100)	681 (m)	683 (100)	655 (m)	657 (100)
680 (vw)	—	—	—	—	—	—	—
702 (m)	702	707 (m)	715 (37)	707 (m)	713 (60)	705 (s)	712 (23)
740 (vs)	738	735 (vs)	745 (32)	732 (vs)	737 (54)	725 (vs)	732 (23)
—	—	757 (w)	—	—	—	—	—
760 (vs)	750	782 (m)	787 (104)	778 (m)	782 (92)	760 (s)	769 (23)

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* 1-Phenylindan displays a medium band at 485 cm^{-1}, whereas this band is absent in the spectrum of 2-phenylindan.[31] Therefore, this band may be characteristic of 1-substituted indans.

† The IR spectrum of solid *trans*-1,2-dibromoindan (KBr pellet) is identical to that taken from the solution in CS_2.

The dibromo compound III displays a very strong IR band at 572 cm^{-1}, which is rather weak in the Raman spectrum, and a strong Raman active band at 657 cm^{-1} which is rather weak in the IR spectrum. Recent investigations carried out in this laboratory[4, 8, 36, 38] on the C–halogen stretching frequencies of vicinal dihalogenides have shown that this combination of bands is highly characteristic of the approximately anti-planar arrangement of the X—C—C—X system (X = Cl or Br); evidence has been accumulated from some fifty compounds, including homocyclic and heterocyclic 5- and 6-membered rings and open-chain compounds. Therefore, the two bands can safely be assigned to the strongly coupled carbon–bromine stretching vibrations of the *diaxial* conformation, the Raman active vibration being due to the symmetrical mode and the strong IR band originating from the asymmetrical mode. The analogous AA bands in the dichloro compound I obey the same intensity rule and are similarly assigned.

The assignment of the axial C–halogen stretching frequencies in the bromochloro compound II is less unambiguous: this derivative displays a strong Raman band at 683 cm^{-1} which is rather weak in the IR spectrum, and two strong IR bands at 605 and 586 cm^{-1} which are rather weak in the Raman spectrum. Either of these bands may be due to the asymmetrical C–halogen stretching vibration. However, as the band at 605 cm^{-1} yields a better agreement of the average C–X stretching frequency with the value calculated from Table 4 (see Table 6), we tentatively assign this mode to the asymmetrical C–halogen vibration.

In Table 6 the axial C–halogen stretching frequencies for compounds I–III are compared with the values calculated from Table 4 (an S_{X_p} type for the C_1–X vibration and an S_{XH} type for the C_2–X mode). The agreement is satisfactory.

TABLE 6. AXIAL C–HALOGEN STRETCHING FREQUENCIES (IR VALUES IN cm^{-1}) IN *trans*-1,2-DIHALOGENOINDANS, COMPARED WITH THE VALUES CALCULATED FROM TABLE 4

Compound	Symm. C–X str.	Asymm. C–X str.	Average	$\Delta\nu$
trans-1,2-dichloroindan	690	662	676	28
calc.			679	
trans-2-bromo-1-chloroindan	681	605	643	76
calc.			652	
trans-1,2-dibromoindan	655	572	613	83
calc.			614	

In the axial conformers of the *trans*-2,3-dihalogenotetrahydropyrans the same types of carbon–halogen stretching vibrations occur: an S_{X_p} type for the C_2–X vibration and an S_{XH} type for the C_3–X mode. The average values of the symmetrical and asymmetrical C–X stretching modes and the $\Delta\nu$ values for these compounds are:[39]

trans-2,3-dichlorotetrahydropyran: 691 cm^{-1}, 93 cm^{-1};
trans-3-bromo-2-chlorotetrahydropyran: 645 cm^{-1}, 110 cm^{-1};
trans-2,3-dibromotetrahydropyran: 611 cm^{-1}, 110 cm^{-1}.

The average frequency values are in excellent agreement with the values found for the corresponding indans; the $\Delta\nu$ values are smaller in the 5-membered ring compounds, especially for the dichloride, which has also been found for the *trans*-1,2-dihalogenocyclopentanes[4] and for the *trans*-3,4-dihalogenotetrahydrofurans.[8]

The weak band at 757 cm^{-1} in the IR spectrum of the dichloro compound I may be assigned to an equatorial C–halogen stretching mode. Although the diequatorial conformer of the bromochloro derivative II is also present, be it in a rather small amount (cf. section A), no band due to the equatorial C–halogen vibrations can be found in the range where the EE modes should appear (650–800 cm^{-1}). However, a number of medium to strong other bands occur in this region, which may well overlap the weak C–halogen bands.

Therefore, we conclude from the infrared and Raman spectra that the diaxial conformer predominates in the *trans*-1,2-dihalogenoindans, which is in accord with the results from the dipole moments and the NMR spectra (section A).

CONCLUSION

The main conformational characteristics of the *trans*-1,2-dihalogenoindans are summarized below:

(1) The results obtained by means of dipole moments, NMR, IR and Raman spectroscopy are consistent.

(2) Two conformers (diaxial and diequatorial) are in dynamic equilibrium. The diaxial form is favoured over the diequatorial one, especially in the dibromo compound, which seems to exist almost exclusively in the diaxial conformation.

(3) The "benzene effect" is found to be unusually small (0·1 kcal/mole) as compared with the values found for other vicinal *trans*-dihalogeno compounds (0·25–0·5 kcal/mole).

EXPERIMENTAL

Syntheses

trans-1,2-*Dichloroindan* (I) was prepared by chlorinating indene employing sulfuryl chloride according to the method described;[40] b.p. 108°/15 mm; n_D^{25} 1·5690 (Lit.[41] b.p. 83–85°/3 mm; n_D^{25} 1·5690). (Found: Cl, 37·8. Calc. for $C_9H_8Cl_2$ (187·07): Cl, 37·9%).

trans-2-*Bromo*-1-*chloroindan* (II) was obtained from indene and N-bromosuccinimide/HCl in CH_2Cl_2 at −20° by the procedure described;[42] b.p. 95°/0·5 mm; n_D^{20} 1·5965. (Found: Hal, 49·3. Calc. for C_9H_8BrCl (231·53): Hal, 49·8%).

trans-1,2-*Dibromoindan* (III) was prepared by the addition of bromine to indene in CH_2Cl_2 at −20°; m.p. 32° from pentane–ether (Lit.[43] m.p. 30–33°). (Found: Br, 58·2. Calc. for $C_9H_8Br_2$ (275·98): Br, 57·9%).

Dielectric measurements. The electric moments were determined by measuring dielectric constants and densities of 5 solns of each compound in benzene and in CCl_4 (molar fraction range 0–0·01) at 25° as

TABLE 7. NUMERICAL DATA OF THE MEASUREMENTS OF THE DIPOLE MOMENTS

Compound	Solvent[a]	α'	β'	P_{2o}	R_D	μ
I	B	5·8970	−0·848	130·46	47·60	2·01
	T	5·1281	+0·170	125·25	47·60	1·95
II	B	5·2953	−1·426	123·40	50·48	1·89
	T	4·6966	+0·015	119·46	50·48	1·84
III	B	3·8334	−2·083	101·92	53·36	1·54
	T	3·6083	−0·148	102·75	53·36	1·55

[a] B = benzene, T = carbon tetrachloride.

described.[3] The total polarization P_{20} was calculated by the method of Halverstadt and Kumler;[44] the dipole moments followed from

$$\mu = 0{\cdot}01281 \times 10^{-18}\,[(P_{20} - R_D)\,T]^{\frac{1}{2}}$$

The 100 Mc/s NMR spectra were taken with a Varian HA-100 NMR spectrometer, using TMS as internal standard. The solns in benzene and in CCl_4 were approximately 10% wt/vol.

The IR spectra were obtained with a Unicam double beam spectrophotometer (SP 100). The spectra were taken from solns (~30 mg/ml) in CS_2.

The Raman spectra were recorded on a photoelectric Hilger and Watts Ramanspectrometer with scanning attachment. Data on the performance of this apparatus have been given elsewhere.[45] The spectra were made with slit widths corresponding to 10 cm^{-1}, scanning speed 60 $cm^{-1}min^{-1}$, time constant 2·5 sec.

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