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CONFORMATION OF NON-AROMATIC RING COMPOUNDS—58[1]

INFRARED AND RAMAN SPECTRA OF *TRANS*-2,3-DIHALOGENOTETRALINS

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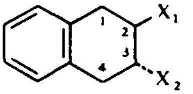
Abstract—The IR and Raman spectra of *trans*-2,3-dichloro-(I), *trans*-2-bromo-3-chloro(II) and *trans*-2,3-dibromotetralin (III) were measured in solution and in the solid state. The spectra from the solutions confirm our previous results from NMR and dipole moments, i.e. that the *diaxial* form strongly predominates in the liquid state. On the other hand, the solid state spectra indicate that the three compounds crystallize in the *diequatorial* conformation.

INTRODUCTION

In a previous paper[2] the conformational features of *trans*-2,3-dichloro- (I), *trans*-2-bromo-3-chloro- (II) and *trans*-2,3-dibromotetralin (III) were discussed on the basis of dipole moments and NMR spectra in several solvents.



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

FIG. 1

The main features are summarized below:

(i) In analogy with cyclohexene the non-aromatic part of the tetralin system is assumed to occur in the half-chair form, the ring dihedral angles ϕ_{12} and ϕ_{23} being about 45° and 60°, respectively. This picture is qualitatively consistent with the X-ray result of a tetrachlorotetralin.[3]

(ii) In solution a conformational equilibrium exists between a diaxially (AA) and a diequatorially (EE) substituted form (Fig. 2), with the diaxial conformer predominating to a large extent (~95% for III in CCl_4, ~80% for I in benzene).

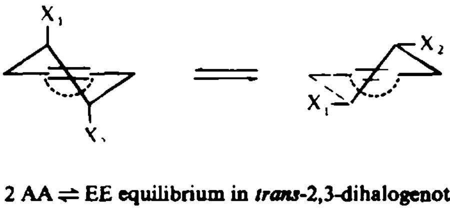


FIG. 2 AA ⇌ EE equilibrium in *trans*-2,3-dihalogenotetralins.

(iii) As normally found with vicinal dihalogenides,[4, 5] down the series from chlorine to bromine an increase in percentage of diaxial conformer is observed, whereas in benzene the conformational equilibrium is shifted towards the more polar diequatorial form to the extent of 0·2–0·3 kcal/mole as compared to solution in carbon tetrachloride ("benzene effect"[4,6]).

In the present paper the conformation of compounds I–III is investigated by means of IR and Raman spectroscopy, in solution as well as in the solid state. The most important part of the spectra for our purpose is the region between 500 and 800 cm^{-1}, where the carbon–halogen stretching vibrations should occur. These frequencies are highly dependent on the geometrical arrangement about the neighbouring C atoms. As has been described earlier,[7,8] each type of C—Br or C—Cl stretching vibration can be specified by P (primary), S (secondary) and T (tertiary halogen), with the atom or atoms in anti-position indicated by a subscript (H, C, O, X (halogen), etc). With each type a specific C—Br or C—Cl stretching frequency is associated. The types pertinent to compounds I–III are S_{XH} (650 cm^{-1} for C—Cl and 596 cm^{-1} for C—Br) and S_{CC} (742 cm^{-1} for C—Cl and 686 cm^{-1} for C—Br). The accuracy of these figures[7] is 5–10 cm^{-1} in systems with "normal" bond angles (viz. chair-shaped rings like cyclohexanes).

For vicinal dihalogenides in the anti (diaxial) conformation two strongly coupled C-halogen stretching vibrations are usually found:[8] an intense Raman band at the higher frequency (ν_{symm}) which is weak in the IR spectrum, and a strong IR band (ν_{asymm}) at a lower wavenumber, which is weak in the Raman spectrum. Even in the antiplanar Br—C—C—Cl systems the C—Br and C—Cl stretching modes appear so strongly coupled that a symmetrical and an asymmetrical band are observed obeying the same rule as the dichlorides and the dibromides. The average value of these two wavenumbers can be predicted[7] by taking the average of the two stretching parameters associated with the "types" described above.

The vibrations of vicinal dihalogenides in the gauche (diequatorial) form are found as medium-intensity bands in the IR as well as in the Raman spectra.[7] The coupling is much weaker than in the anti system.

RESULTS

Fig. 3 shows schematically the IR and Raman spectra of I, II and III in the solid state and in solution between 500 and 800 cm^{-1}. The exact wavenumbers for the various spectra, together with the intensities, are collected in the experimental part.

Spectra in solution

The IR spectra were taken in CS_2, the Raman spectra in THF (which has no Raman bands in this region). The Raman spectra in CCl_4 solution between 500 and 730 cm^{-1} were identical to those taken in THF.

The dibromo compound III displays a very strong IR band at 550 cm^{-1}, which is weak in the Raman spectrum, and a strong Raman active band at 637 cm^{-1}, which is weak in the IR. According to the picture described above these two bands may safely be assigned to the C—Br stretching vibrations of the diaxial form.

The band at 584 cm^{-1} in III is also rather strong in the Raman spectrum and weak in the IR, but in I and II a band at about the same frequency is found, therefore ruling out the possibility that this band should represent the symmetrical C—Br stretching band in III (cf. also Table 1).

The analogous AA bands in the bromochloro (II) and in the dichloro (I) derivatives are similarly assigned (Table 1). In Table 1 the axial C-halogen stretching frequencies

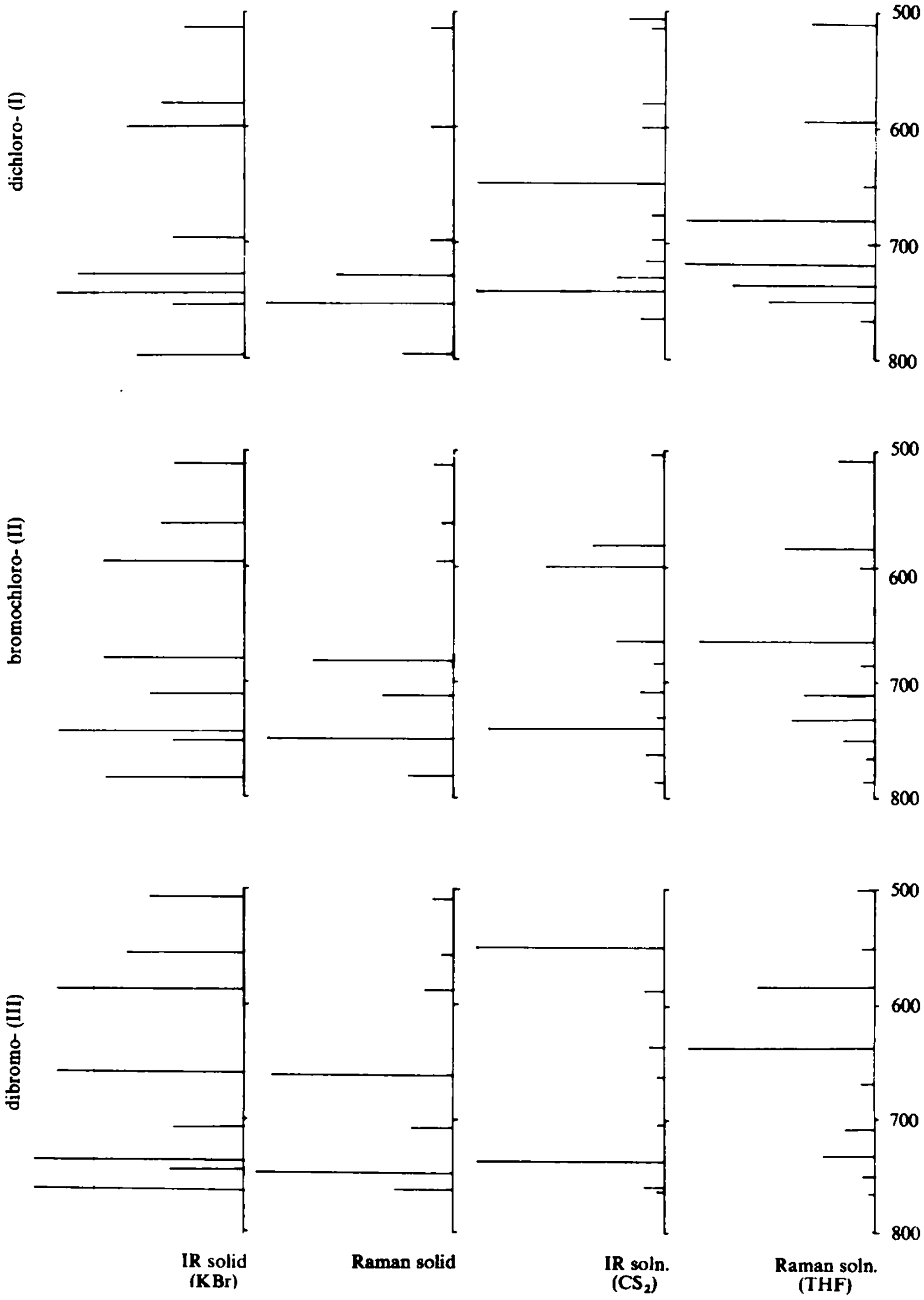


FIG. 3 IR and Raman spectra of *trans*-2,3-dihalogenotetralins between 500 and 800 cm^{-1}.

for I–III are compared with those for the corresponding *trans*-1,2-dihalogenocyclohexanes[8] (also S_{XH} types) and with the values accepted for the S_{XH} vibrations. The agreement is satisfactory.

TABLE 1. AXIAL C-HALOGEN STRETCHING FREQUENCIES (IR VALUES IN CM^{-1}) IN *trans*-2,3-DIHALOGENOTETRALINS, COMPARED WITH THE VALUES FOR *trans*-1,2-DIHALOGENOCYCLOHEXANES

Compound	Symm. C—X str.	Asymm. C—X str.	Average	Δv
tr-2,3-Dichlorotetralin	676	649	663	27
tr-1,2-Dichlorocyclohexane	690	610	650	80
S_{XH} (chloro)			650	
tr-2-Bromo-3-chlorotetralin	664	600	632	64
tr-1-Bromo-2-chlorocyclohexane	665	580	623	85
S_{XH} (bromochloro)			623	
tr-2,3-Dibromotetralin	636	550	593	86
tr-1,2-Dibromocyclohexane	653	542	597	111
S_{XH} (bromo)			596	

Depolarization measurements of the strong symmetrical C-halogen stretching Raman bands yielded $\rho = I_{\perp}/I_{//} = 0{\cdot}20$, 0·19 and 0·20 for compounds I, II and III, respectively. As expected, these bands are thus highly polarized. Similar measurements[9] on the symmetrical C—Br and C—Cl stretching vibrations in some other vicinal dihalogenides in the anti form (ethanes, dibromocyclohexane, -cyclopentane and -tetrahydrofuran) yielded ρ-values ranging from 0·15 to 0·21.

From Table 1 it appears that the Δv values for the tetralins are rather smaller than for the corresponding cyclohexanes, especially in the case of the dichloro compound. Such unusual low Δv values for the dichlorides have thus far been found only in 5-membered ring compounds, i.e. in *trans*-1,2-dichlorocyclopentane[10] (36 cm^{-1}), *trans*-1,2-dichloroindan[11] (28 cm^{-1}), *trans*-3,4-dichlorotetrahydrofuran[12] (25 cm^{-1}) and *trans*-2,3-dichlorotetrahydrofuran[13] (20 cm^{-1}).

From the spectra in solution, no assignment can be made for the equatorial C-halogen stretching vibrations, as the diequatorial form has only a small molar fraction in the equilibrium mixture (see previous section) and as several weak bands occur in the region in question (650–800 cm^{-1}).

Solid state spectra

The IR spectra were taken from KBr-discs and the Raman spectra from powdered samples.

Inspection of Fig. 3 reveals that the characteristic pattern of the C-halogen stretching vibrations due to the diaxial form *is not present* in the solid state spectra of either of the three compounds.

In fact, at about the same frequency of the asymmetrical C—Br stretching vibration in the liquid state spectra of II and III, a band is also observed in the solid state spectra. However, this band is certainly due to another mode, as no band is found at the wavenumber of the symmetrical C-halogen stretching vibrations of I, II and III and of the asymmetrical one of I.

The dibromo compound III displays both in the IR and in the Raman spectrum in the solid state a strong band at 660 cm^{-1}, which is found as a very weak mode in the spectra in solution. This band might be attributed to the equatorial C—Br stretching band, and it seems, therefore, that compound III crystallizes in the *diequatorial* conformation. In compounds I and II the spectral pattern in the solid state between 650 and 800 cm^{-1} is also very different from that in solution, but due to the large number of strong bands close to each other it is difficult to assign one of them to a C-halogen stretching band. However, taking the absence of the axial C—X stretching bands into account, it may be concluded that also these compounds exist in the *diequatorial* conformation in the solid state.

With these compounds we have, therefore, the situation that in solution the diaxial form predominates very strongly, whereas in the solid state the diequatorial form is found. A similar situation exists in 2-bromo- and 2-chlorocyclohexanone,[14] which crystallize in the equatorial conformation, whereas the axial form of the former has a molar fraction of 0·9 in diluted CCl_4 solution.[5, 15] In the corresponding *trans*-1,2-dihalogenocyclohexanes,[8] the bromochloro and dichloro compounds (in solution only slightly more stable in the diaxial form) crystallize in the diequatorial conformation, whereas the dibromo derivative crystallizes in the (most stable) diaxial form.

CONCLUSION

From the IR and Raman spectra between 500 and 800 cm^{-1} of *trans*-2,3-dihalogenotetralins the following conclusions appear:

(a) In solution strong bands characteristic of the C-halogen stretching modes of the diaxial form are found. This is in agreement with earlier conclusions from NMR and dipole moment data,[2] i.e. that the AA form strongly predominates in solution.

(b) The average of the symmetrical and the asymmetrical C—X stretching mode is in good agreement with the value accepted for the S_{XH} type. The unusual low value for $\Delta\nu$ in the dichloro compound was thus far only found in the case of vicinal diaxial dichlorides of 5-membered rings.

(c) The solid state spectra indicate that the three compounds do not crystallize in the diaxial conformation that predominates in solution, but rather in the diequatorial form. An analogous behaviour is found with some other cyclic halogeno-substituted compounds.

EXPERIMENTAL

The compounds were synthesized as previously described.[2]

The IR spectra were obtained with a Perkin–Elmer 225 grating IR spectrometer. The spectra were taken from solutions (~30 mg/ml) in carbon disulfide, and from KBr discs. The wavenumbers in the range 400–1600 cm^{-1} are presented below:

trans-2,3-Dichlorotetralin (CS_2): 430 (m), 462 (w,b), 482 (vw), 506 (w), 514 (vw), 579 (w), 600 (w), 649 (vs), 676 (w), 697 (w), 715 (w), 730 (sh), 742 (vs), 765 (w), 802 (w), 855 (sh), 868 (s), 900 (m), 919 (w), 929 (w), 948 (sh), 959 (vs), 988 (w), 1014 (w,b), 1039 (w), 1108 (m), 1114 (sh), 1154 (vw), 1163 (vw), 1181 (w), 1190 (vw), 1216 (s), 1248 (w), 1260 (m), 1272 (w), 1289 (vw), 1344 (m), 1360 (vw), 1401 (m);

Idem (KBr): 431 (s), 450 (vw), 460 (m,d), 514 (w), 579 (w), 599 (s), 696 (w), 727 (vs),744 (vs), 754 (sh), 798 (m), 861 (sh), 872 (m), 900 (vs), 920 (m), 950 (m), 1024 (vw), 1030 (vw), 1038 (w), 1053 (vw), 1108 (m), 1153 (vw), 1160 (sh), 1198 (m), 1212 (m), 1250 (m), 1275 (w), 1290 (m), 1300 (w), 1335 (vw), 1350 (w), 1430 (m,d), 1450 (m), 1486 (s), 1500 (m), 1581 (m), 1604 (vw).

trans-2-*Bromo-3-chlorotetralin* (CS_2): 430 (m), 449 (vw), 465 (vw), 479 (w), 503 (w), 581 (s), 600 (vs), 664 (m), 683 (w), 708 (w), 730 (sh), 740 (vs), 762 (w), 786 (m), 855 (sh), 864 (s), 894 (w), 917 (vw), 929 (w), 959 (s), 988 (w), 1018 (w), 1040 (w), 1108 (sh), 1111 (m), 1155 (w), 1174 (m), 1212 (m), 1240 (w), 1260 (w), 1268 (w), 1288 (vw), 1304 (vw), 1343 (m), 1361 (vw), 1403 (m).

Idem (KBr): 430 (m), 448 (m), 464 (w), 511 (w), 563 (w), 596 (s), 680 (s), 711 (m), 743 (vs), 752 (sh), 783 (s), 859 (m), 869 (m), 893 (m), 918 (m), 950 (m), 1019 (vw), 1026 (vw), 1038 (w), 1048 (vw), 1108 (w), 1154 (vw), 1178 (s), 1205 (m), 1245 (w), 1271 (w), 1289 (m), 1298 (w), 1334 (w), 1346 (w), 1429 (m,d), 1450 (w), 1486 (s), 1500 (w), 1583 (m), 1606 (vw).

trans-2,3-*Dibromotetralin* (CS_2): 433 (m), 476 (w), 495 (w), 550 (vs), 588 (vw), 636 (w), 662 (vw), 704 (vw), 737 (vs), 759 (w), 763 (sh), 859 (s), 888 (vw), 930 (m), 960 (vs), 988 (m), 1018 (w,b), 1041 (m), 1109 (s), 1158 (s), 1171 (sh), 1212 (s), 1224 (m), 1260 (m), 1287 (vw), 1305 (w), 1342 (m), 1349 (sh), 1364 (w), 1408 (m).

Idem (KBr): 421 (m), 439 (s), 455 (m), 508 (m), 556 (m), 588 (vs), 660 (s), 708 (w), 738 (vs), 746 (sh), 763 (vs), 856 (m), 862 (sh), 885 (m), 912 (m), 948 (m), 1013 (vw), 1019 (vw), 1035 (w), 1104 (w), 1152 (sh), 1175 (s), 1212 (vw), 1240 (vw), 1262 (w), 1283 (w), 1293 (sh), 1322 (vw), 1329 (vw), 1339 (vw), 1346 (vw), 1426 (m,d), 1450 (w), 1483 (m), 1498 (m), 1579 (m), 1600 (vw).

The Raman spectra were recorded on a Cary 81 spectrometer with He/Ne laser source. The spectra were taken from solutions (~20%) in tetrahydrofuran and in carbon tetrachloride, and from powdered samples. The depolarization ratios were determined in CCl_4 solution using UV cells according to the method described.[16] The 314 and 459 cm^{-1} bands of CCl_4 were used for calibration, yielding $\rho = 0{\cdot}76$ and 0·01, respectively. The ρ values are reproducible to ±0·02. The wavenumbers (for the solid state spectra in the range 400–1600 cm^{-1}) are presented with the measured peak intensities on the usual relative scale (intensity of the strongest line = 100).

trans-2,3-*Dichlorotetralin* (solid): 436 (7), 465 (26), 515 (8), 600 (8), 698 (14), 728 (62), 752 (100), 796 (27), 865 (7,b), 900 (13), 919 (4), 955 (vw), 984 (vw), 1038 (50), 1053 (sh), 1105 (7), 1156 (24), 1199 (30), 1214 (9), 1276 (15), 1291 (9), 1298 (9), 1327 (vw), 1335 (vw), 1349 (7), 1435 (26), 1582 (13), 1604 (9).

Idem (THF): 510 (33), 650 (6), 594 (39), 679 (100), 700 (vw), 718 (100), 736 (78), 750 (56), 766 (vw), 802 (11).

Idem (CCl_4): 508 (33), 650 (6), 592 (39), 678 (100), 696 (vw), 715 (100), 735 (45).

trans-2-*Bromo-3-chlorotetralin* (solid): 433 (15), 448 (27), 464 (24), 512 (8), 562 (6), 596 (8), 682 (71), 712 (42), 750 (100), 781 (29), 861 (15), 896 (18), 918 (6), 954 (vw), 1038 (73), 1102 (9), 1156 (33), 1178 (18), 1198 (33), 1245 (vw), 1271 (15), 1289 (9), 1296 (9), 1334 (6), 1346 (9), 1433 (33), 1582 (18), 1605 (9).

Idem (THF): 507 (20), 600 (7), 583 (50), 664 (100), 684 (7), 710 (40), 731 (47), 750 (17), 765 (vw), 785 (7).

Idem (CCl_4): 503 (18), 600 (5), 582 (55), 665 (100), 683 (5), 709 (47), 730 (41).

trans-2,3-*Dibromotetralin* (solid): 424 (16), 443 (12), 458 (17), 509 (7), 556 (4), 588 (10), 662 (76), 708 (16), 748 (100), 762 (22), 790 (2), 859 (10), 888 (16), 914 (6), 953 (2), 1022 (5), 1038 (52), 1095 (7,d), 1154 (24), 1178 (19), 1196 (21), 1263 (12), 1287 (9), 1296 (7), 1332 (5), 1345 (7), 1430 (24), 1581 (12), 1602 (10).

Idem (THF): 500 (9), 550 (6), 584 (64), 637 (100), 667 (6), 708 (16), 732 (28), 750 (6), 765 (vw).

Idem (CCl_4): 498 (10), 550 (5), 582 (57), 637 (100), 664 (5), 704 (17), 730 (29).

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