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Abstract

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Raman Spectra of Alkyl and Alkenyl Derivatives of 1,1-Dichlorocyclopropane

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It is known that cyclopropane and its derivatives, in their chemical and physical properties, are similar to olefins ([1–3]). The analogy between a double bond and the cyclopropane ring is also manifested in the fact that the latter is capable of entering into conjugation, for example, with a double bond and with an aromatic ring ([4,5]). Modern theory explains these features in the behavior of the three-membered ring by the closeness of the hybridization of the valences of the carbon atoms of the ring to sp^2. As a result, one of the valences used to form the bonds in the ring has to a considerable degree p-character, i.e., is similar to that which participates in the formation of the π-bond in ethylene ([1,2]).

It has recently been shown that conjugation of the three-membered ring with unsaturated groups depends substantially on their mutual orientation, and in such a way as if the "share" of the electron cloud responsible for the conjugation effect were located in the plane of the ring, perpendicular to the plane of the methylene groups ([6,7]). Formally, this part of the electron cloud may be regarded as a π-electron cloud, on the basis of an analogous dependence of conjugation on configuration for truly conjugated systems.

It was of interest to determine in what direction the properties of the three-membered carbon ring change in the presence of substituents exhibiting a strong inductive effect and, consequently, capable of changing the state of hybridization of the valences of the carbon atoms of the ring. Existing theoretical work makes it possible to draw certain preliminary conclusions about the direction of the expected effects. Thus, according to Walsh ([8]) and Bent ([9]), replacement of one of the groups X in CX_4 by a more electronegative group Y leads to an increase in the p-character of the $C—Y$ bond and the s-character of the $C—X$ bonds. Consequently, it could be expected that replacement of hydrogen atoms of the cyclopropane ring by electronegative substituents would lead to a weakening of the p-character of the molecular orbitals of the ring, i.e., to a weakening of the degree of its unsaturation.

In order to test this assumption, we undertook a study of the Raman spectra of several alkyl and alkenyl derivatives of 1,1-dichlorocyclopropane, as well as 1,1-dichloro-2-phenylcyclopropane. Some of the compounds are structurally

similar to previously studied hydrocarbons, in which conjugation of the three-membered ring with a double bond was found, but in the ring they have two chlorine atoms as substituents. The dichlorocyclopropanes were obtained by the method described earlier ([10]), through the interaction of chloroform and potassium tert-butylate with the corresponding olefin, taken in excess ([11]). The reaction products were distilled on a column with an efficiency of 20 theoretical plates.

The method of obtaining the Raman spectra and of processing them (measurement of frequencies and intensities) was described in previous communications ([6,12]).

1,1-Dichloro-2-ethylcyclopropane (I). B.p. 122.3°/737 mm; n_D^{20} 1.4463; d_4^{20} 1.1082.

$\Delta\nu$: 111(20), 120(10), 249(32), 270(39), 298(15, ϕ)*, 314(50), 352(12), 367(16), 426(16), 462(150), 521(66), 557(15), 709(20), 736(24), 752(24), 763(26), 777(17), 796(23), 859(5), 893(23, sh), 925(2), 955(14), 969(14), 1002(5, sh), 1041(7), 1050(14), 1097(7), 1123(6), 1169(7),

* Designations: sh –broad, r –sharp, ϕ –background, db –double.

Table 1

Molar integral intensities of double-bond lines in the spectra of derivatives of 1,1-dichlorocyclopropane

Compound	C=C line, cm^{-1} (in parentheses I_M^∞)	Phenyl-ring line, ~ 1600 cm^{-1} (I_∞^M)
C–C–C=C, with CCl_2 cyclopropane ring	1638 (700)	–
C–C–C=C, methyl-substituted CCl_2 cyclopropane ring	1640 (580)	–
C–C–C–C=C, with CCl_2 cyclopropane ring	1640 (340)	–
C–C–C=C ([4]), cyclopropane ring	1640 (660)	–
α-olefins, R–C=C ([16])	1642 (300–400)	–

Compound	C=C line, cm^{-1} (in parentheses I_M^∞)	Phenyl-ring line, ~ 1600 cm^{-1} (I_∞^M)
Phenyl-C—C, with CCl_2 cyclopropane ring	–	1606 (820)
Phenyl-C—C ([4]), cyclopropane ring	–	1605 (1150)
Monoalkylbenzenes ([16])	–	1605 (300–500)

1226(21, broad), 1265(6), 1295(2), 1316(7), 1332(5), 1381(11), 1447(22, broad), 1638(4), 2875(100, doublet), 2911(60, f), 2937(130), 2970(50), 3008(150), 3088(60).

1,1-Dichloro-2-vinylcyclopropane (II). B.p. 68.0°/164 mm; n_D^{20} 1.4732; d_4^{20} 1.1529.

$\Delta\nu$: 96(40, broad, doublet), 136(50, broad), 267(62, broad), 306(10), 319(92, p), 350(21), 391(10), 407(41, broad), 470(150), 512(50, broad), 552(5), 674(16), 766(43), 793(64), 825(4, broad), 878(34, broad), 920(15), 932(15), 985(15, f), 996(62), 1020(25), 1047(28), 1071(3), 1090(3), 1115(7, broad), 1162(6), 1196(25), 1220(90), 1295(60), 1323(10), 1354(3), 1432(50, broad), 1612(8), 1638(210), 1655(7), 2836(10), 2876(10), 2936(30), 2992(70, f), 3015(270, broad), 3092(100).

1,1-Dichloro-2-methyl-2-ethylcyclopropane (III). B.p. 145.7°/745 mm; n_D^{20} 1.4557; d_4^{20} 1.0952.

$\Delta\nu$: 111(35, broad, doublet), 180(20, broad), 226(12, broad), 258(27), 276(32), 310(38), 322(36), 345(18), 357(17), 372(12), 432(24, broad, doublet), 467(180), 530(78), 595(21), 689(47), 714(47), 759(43), 784(2), 862(34), 884(16), 941(19), 1001(16), 1019(20), 1034(15), 1072(7), 1096(9), 1118(9), 1240(11), 1271(18), 1317(7), 1353(10), 1385(8), 1427(10), 1444(38), 1460(38), 2744(10), 2880(90, doublet), 2907(60, f), 2936(170), 2971(100, f), 3002(140), 3080(50).

1,1-Dichloro-2-methyl-2-vinylcyclopropane (IV). B.p. 72.6°/66 mm; n_D^{20} 1.4783; d_4^{20} 1.1320.

$\Delta\nu$: 195(20, broad), 219(3), 260(21), 296(46), 342(41), 375(15), 420(29), 431(28), 474(170, broad), 520(13), 530(12), 571(3), 680(46), 691(33), 722(35), 766(33), 799(3), 838(26), 864(3), 895(28), 920(7, broad), 948(35), 993(6, broad), 1023(30), 1047(18), 1096(11), 1236(3, f), 1265(5, f), 1275(26), 1292(25), 1315(21), 1380(4), 1419(54), 1457(14, broad), 1616(3, f), 1640(96), 2836(30), 2882(20), 2937(60), 2971(40, f), 3006(140), 3026(50), 3089(60).

4-(2,2-Dichlorocyclopropyl)-butene-1 (V). B.p. 78.5°/33 mm; n_D^{20} 1.4662; d_4^{20} 1.0814.

$\Delta\nu$: 185(10, broad, f), 219(10, broad, f), 232(10, broad, f), 273(36, broad), 292(36, broad), 312(20), 349(3), 373(5), 417(8, broad), 461(66, broad), 508(10, f), 520(39), 550(21), 590(3), 741(30), 750(28), 773(16), 811(19), 870(4), 890(17), 915(14), 944(10), 952(10), 975(2), 992(5), 1013(2), 1035(7), 1049(6), 1120(2), 1188(2), 1213(15, f), 1226(27), 1255(2), 1295(32, broad, doublet), 1323(2), 1335(2), 1381(14), 1415(27), 1439(20, broad), 1640(74), 2855(20), 2887(10, f), 2915(50), 2945(40, f), 2982(30, f), 3005(90, broad), 3084(50).

1,1-Dichloro-2-phenylcyclopropane (VI). B.p. 83.5°/5 mm; n_D^{20} 1.5525; d_4^{20} 1.2263.

$\Delta\nu$: 209(82), 236(64), 289(100), 307(50), 343(2), 403(15, broad), 475(92, broad), 548(66), 590(25), 622(56, p), 733(56), 753(42), 777(30), 802(4, broad), 837(5, broad), 867(20, broad), 932(52), 951(86), 1003(410, p), 1030(86), 1056(31, broad), 1084(10), 1097(5), 1117(24), 1136(7), 1158(29), 1195(34), 1230(64), 1251(3), 1294(18), 1313(16), 1330(5), 1358(35, broad), 1371(40, broad), 1394(5), 1425(42), 1452(9), 1475(2), 1500(20), 1527(3), 1584(24), 1606(165), 1628(10), 2823(5), 3010(190, broad), 3032(20), 3047(30), 3063(240), 3088(60).

Considering the data obtained, it can be seen that in spectrum V, in which the double bond is separated from the three-membered ring by two methylene groups, the frequency and intensity of the double-bond line have the usual values —the same as in the spectra of α-olefins (Table). At the same time, in spectra II and VI, where the three-membered ring is located next to the vinyl group or the benzene ring, a substantial enhancement of the C=C lines or of the 1600 cm^{-1} line is observed, indicating conjugation of the three-membered ring with the double bond or with the benzene ring. We note that spectrum VI also has other characteristic features of conjugated systems involving a benzene ring: the presence of an intense line in the region of 1230 cm^{-1}, the appearance of a line near $\sim$ 1500 cm^{-1}, etc. ([6,13]).

The magnitude of the effect in spectrum VI is noticeably smaller than for the corresponding hydrocarbon—the difference between the values of $I_\infty^M(1600)$ lies outside the limits of error in measuring the integral intensities of the lines (10%). In the other cases the magnitude of the effect is the same as in the spectra of the corresponding hydrocarbons. The somewhat smaller value of I_∞^M(C=C) in spectrum IV as compared with II could have been due to the steric influence of the methyl group, which displaces the vinyl group from the position most favorable for conjugation with the three-membered ring.

Table 2

Frequency and intensity of the lines of the stretching vibrations of the CCl_2 group

Compound	$\nu^{sym}_{CCl_2}$	$\nu^{asym}_{CCl_2}$ (assignment)
C–C–C–Cwith CCl_2 on the cyclopropane ring	462 (150)	521 (66)
C–C–C=Cwith CCl_2 on the cyclopropane ring	470 (150)	512 (50, sh)
C–C–C–Cwith CCl_2 on the cyclopropane ring and a C substituent	467 (180)	530 (78)
C–C–C=Cwith CCl_2 on the cyclopropane ring and a C substituent	474 (170, sh)	520 (13),530 (12) *
C–C–C–C–C Cwith CCl_2 on the cyclopropane ring	461 (66, sh)	508 (10, f),520 (39),550 (21) *
benzene ring–C–Cwith CCl_2 on the cyclopropane ring	475 (92, sh)	548 (66)

* One of the indicated lines.

On the whole these data show that, in the cases studied, the influence of chlorine atoms on the conjugation of the three-membered ring with a double bond or a phenyl group is small, i.e., replacement by chlorine atoms of the hydrogen atoms of the three-membered ring has little effect on the degree of its unsaturation. This conclusion, which should be regarded as preliminary and requiring additional verification on other objects,* indicates either a small change in the hybridization of the valences of the carbon atom under the influence of chlorine atoms, or a weak transmission of this effect through the ring to the carbon atom bonded to the vinyl or phenyl group.

In the spectra of all the substances there is an intense and fairly broad line near 460-475 cm^{-1}, which is apparently due to the symmetric stretching vibration of the CCl_2 group (Table 2). It is more difficult to isolate in the spectrum the line of the asymmetric stretching vibrations of CCl_2; it should have a higher frequency. It is possible that one of the fairly intense lines located in the region 510-550 cm^{-1} should be assigned to this type of vibration. From the few Raman spectra known in the literature for compounds containing a CCl_2 group, it is seen that stretching vibrations of the bonds

* We note that the chemical data nevertheless indicate a greater stability of the three-membered ring in 1,1-dichlorocyclopropane derivatives as compared with

the corresponding hydrocarbons with respect to hydrogenolysis of the ring, isomerization of it in the presence of silica gel under conditions of chromatographic adsorption analysis, and cleavage of the ring under the action of mercury salts.

C—Cl have, in these cases, somewhat higher frequencies. Thus, in 2,2-dichloropropane, which can to a certain extent be regarded as a model compound with respect to the 1,1-dichlorocyclopropane ring, the frequencies of the symmetric and asymmetric stretching vibrations of the CCl_2 group are 559 and 653 cm^{-1}, respectively^(14). In 2,2-dichlorobutane the frequencies of these vibrations are 544(566?) and 642(688?) cm^{-1}^(14). Spectra are also known for a number of polychloro-substituted alkanes. However, in these cases it is not possible to assign the lines of the CCl_2 groups unambiguously. Unfortunately, we have not found in the literature spectra of cycloalkanes bearing groups with which our data could best be compared. From the available material one can nevertheless conclude that the frequencies $\nu^{\text{sym}}_{\text{C-Cl}}$ and $\nu^{\text{asym}}_{\text{C-Cl}}$ of the CCl_2 group in the spectra of 1,1-dichlorocyclopropane derivatives are lowered, in comparison with dichloroalkanes of similar structure, by several tens of cm^{-1}. This effect is somewhat unexpected. The point is that the frequencies of the stretching vibrations of exocyclic bonds in three-membered rings are, as a rule, considerably higher than the frequencies of the corresponding bonds in unstrained systems. As an example one may cite the values of $\nu_{\text{C-H}}$ in the spectra of cyclopropane derivatives, which are raised by approximately 100-120 cm^{-1} in comparison with other cycloalkanes and the aliphatic series. This increase is consistent with the enhanced *s*-character of the exocyclic orbitals of the three-membered ring, which leads to strengthening of the corresponding bonds. Therefore, if one proceeds from the assumption that the C—Cl bonds in 1,1-dichlorocyclopropane derivatives also obey the indicated regularity, one should have expected, other things being equal, an increase in their frequencies. The supposition of strengthening of the C—Cl bonds in 1,1-dichlorocyclopropane derivatives, as compared with chloroalkanes, can be correlated with a decrease in their mobility, as evidenced by the available chemical data. Thus, they are not hydrolyzed under the action of alkalis, are not cleaved by metallic sodium or silver nitrate, etc.^(15). Then, in order to reconcile this supposition with the results of the spectral study, it remains to conclude that the observed decrease in the frequencies of CCl_2 in 1,1-dichlorocyclopropane and its derivatives is a consequence of the purely mechanical interaction of the C—Cl bonds of the CCl_2 group with the three-membered ring. To verify this conclusion it is necessary to solve the problem of the vibrations of the 1,1-dichlorocyclopropane ring. The latter cannot be solved at present because of the absence of the data required for the calculation.

In conclusion, let us note that in the region of the frequencies of the C—H stretching vibrations an intense line of the C—H bond of the three-membered ring is clearly visible (~3000 cm^{-1})^(4). Its identification is unambiguous in the spectra of compounds that do not contain double bonds in their structure (I, III).

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