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Raman Spectra of Cyclopentane and Some of its Monoalkyl Derivatives

BY E. J. ROSENBAUM AND H. F. JACOBSON

Practically no work has been done so far on the Raman spectra of hydrocarbons related to cyclopentane. This is undoubtedly due to difficulty in obtaining these compounds in a sufficiently pure state. In order to make comparisons with other rings having side chains attached, we have examined the Raman spectra, including some semi-quantitative polarization data, of pure samples of cyclopentane and nine of its monoalkyl derivatives. Only one of these derivatives, methylcyclopentane, has been reported previously.[1] Data for analogous benzene and cyclohexane derivatives will be published shortly.

Experimental

We were particularly fortunate in having available for our work the important series of compounds synthesized by Professor V. Ipatieff and Dr. H. Pines.[2] We are greatly indebted to them for their kindness in lending us these samples. Physical constants are given[2] for all the samples used except cyclopentane and methylcyclopentane. For these two compounds we found the values: cyclopentane, b. p. 49–49.5°, n_D 1.4068; methylcyclopentane, b. p. 71.0°, n_D 1.4100.

The spectroscopic equipment was the same as in earlier work.[3] The polarization apparatus was patterned after that of Reitz.[4] It consisted essentially of a Wollaston prism polarizer and a calcite wedge depolarizer. This combination has the advantage that both polarized components of the scattered light are photographed simultaneously while only unpolarized light enters the spectrograph. The principal disadvantage of this type of polarization apparatus is the small intensity of the light which reaches the spectrograph. This necessitates the use of low dispersion and relatively long exposure time.

Data

The symbols used in presenting the data are the same as in reference 3 with the addition that P and dp represent polarized and depolarized, respectively.

Cyclopentane.—207(0) (k, e), 288(1) (k, e), 712(0) (k, e), 888(10, P) (k, i, e), 1032(5, dp) (k, e), 1298(1) (k, e), 1448(5d, dp), (k, e), 1482(1d) (k, e), 2869(10, P) (q, p, k, i, e), 2901(4, dp) (q, p, k, i, e), 2943(7vd, dp) (q, p, k, i, e), 2970(6, dp) (q, p, k, i, e).

Methylcyclopentane.—227(2) (k, e), 314(1) (k, e), 344(2d) (k), 430(1d, dp) (k, e), 534(4, P) (k, ±e), 799 (0vvd) (k, e), 845(1vd) (k, e), 894(6, P) (k, i, e), 980(1vd) (k, e), 999(0vvd) (k, e), 1021(1d) (k, e), 1131(0d) (k, e), 1192(0d) (k, e), 1277(1d) (k, e), 1318(1) (k, e), 1352(3) (k, e), 1427(2s) (k, e), 1453(6 unsym, dp) (k, e), 1480(1d) (e), 2728(1) (q, p, k, e), 2859(7d, P?) (q, k, e), 2871(10) (q, p, k, i, e), 2912(2d) (k, e), 2928(9d, dp) (q, p, k, e), 2961(9d, dp) (q, k, i, e).

Ethylcyclopentane.—353(1vd) (k), 393(2d, dp) (k, e), 423(1d) (e), 761(1vvd) (k, e), 845(1) (e), 857(2d) (k, e), 892 (5d, P) (k, e), 940(1vd) (k, e), 1012(2vd) (k, e?), 1023(3) (k, e), 1038(2) (k, e), 1090(1d) (k, e), 1131(1d) (k, e), 1191 (1) (e), 1290(1) (k, e), 1334(2d, dp) (k, e), 1360(3, dp) (k, e), 1449(5d, dp) (k, e), 2736(1d) (k, e), 2856(10, P) (k, i, e), 2874(10, dp) (q, k, i, e), 2908(3d) (p, k, e), 2937(9d,dp) (p, k, i, e), 2965(8d, dp) (q, p, k, i, e).

***n*-Propylcyclopentane.**—318(3d unsym, P?) (k, i, ±e), 364(2d) (k, ±e), 444(0d) (k, e), 542(0d) (e), 741(1d, dp) (k, e), 836(3d) (k, e), 874(4d, P) (k, e), 896(8, P) (k, i, e), 949(1d, dp) (k, e), 982(1d) (e), 1036(4d, dp) (k, e), 1127 (3d, dp) (k, e), 1185(1vd) (k, e), 1235(1, dp) (k, e), 1300 (4, dp) (k, e), 1348(3, dp) (k, e), 1366(2) (e), 1387(1) (k, e), 1438(2d) (k, e), 1446(10d, dp) (k, i, e), 1477(1vvd) (k, e), 2843(7) (k, i, e), 2861(10, P) (p, k, i, e?), 2871(10vd) (q, k, i, e), 2912(3) (k, e), 2937(9d, dp) (p, k, i, e), 2962(9d, dp) (p, k, i, e).

Isopropylcyclopentane.—334(5d, P?) (k, ±e), 350(0d) (e), 419(4) (k, e), 440(0) (e), 465(6, dp) (k, ±e), 847(3vvd, dp) (k, e), 875(2) (k, e), 895(8d, P) (k, e), 955(4d, dp) (k, e), 983(2vd) (k, e), 1033(3d, dp) (k, e), 1137(4, dp) (k, e), 1166(3vd), (k, e), 1203(3, dp) (k, e), 1302(1vvd) (k, e), 1321(4, dp) (k, e), 1357(4, dp) (k, e), 1384?(1vvd) (e), 1447 (10, dp) (k, e), 1464(3, dp) (k, e), 2852(8, P) (q, k, e), 2871 (10, P?) (p, k, i, e), 2906(4d) (q, k, e), 2935(6vvd, dp) (p k, i, e), 2961(10vvd,dp) (q, p, k, i, e).

***n*-Butylcyclopentane.**—300(4, P) (k, ±e), 321?(0vd) (k, e), 355?(0vd) (k, e), 778(0d) (k, e), 845(1d, dp) (k, e), 875(2, dp) (k, e), 894(5, P) (k, i, e), 932(0) (k, e), 963(1d, dp) (k, e), 1024(2, dp) (k, i, e), 1041(1) (k, e), 1060(1) (k, e), 1129(2) (k, e), 1300(4d, dp) (k, e), 1438(5, dp) (k, e), 1449 (7, dp) (k, i, e), 2846(2) (k, e), 2856(5, P) (q, p, k, i, e), 2872 (8, dp) (p, k, i, e), 2915(2) (p, i, e), 2938(8, dp) (p, k, i, e), 2962(8, dp) (p, k, i, e).

***s*-Butylcyclopentane.**—331(4) (k, e), 346(1) (k, e), 383(2) (k, e, i), 409(1) (k, e), 428(1) (k, e), 483(2) (k, e), 509(1) (k, e), 769(2) (k, e), 831(3) (k, e), 861(4) (k, e), 897 (8, P) (k, e), 935(1d) (k, e), 944(1d) (k, e), 995(1) (k, e), 1028(5) (k, e), 1041(3) (k, e), 1068(1) (k, e), 1089(0) (k, e), 1143(2) (k, e), 1191(2) (k, e), 1280(2) (k, e), 1311(2) (k, e), 1326(2, dp) (k, e), 1344(1) (k, e), 1363(2, dp) (k, e), 1381 (1) (k, e), 1449(5d, dp) (k, e), 1464(2vvd) (k, e), 2854(8, P) (k, i, e), 2873(10d) (q, k, i, e), 2911(4) (k, e), 2938(8, dp) (p, k, i, e), 2962(10d, dp?) (q, k, i, e).

***t*-Butylcyclopentane.**—298(1) (k?, ±e), 337(4, P?) (k, ±e), 385(0vd) (k, e), 444(2d, dp) (k, e), 502(2d, dp) (k, e), 539(3d, dp) (k, e), 715(2vvd, dp) (e), 764(1vd) (e), 808 (1vd) (e), 853(2vd) (k, e), 899(5, P) (k, i, e), 927(5, dp) (k, e), 975(0d) (k, e), 1018(2) (k, e), 1138(2) (k, e), 1217 (1vd) (k, e), 1255(4) (k, e), 1317(2, dp) (k, e), 1334(1) (e),

(1) Kohlrausch, Reitz and Stockmair, *Z. physik. Chem.*, **B32**, 229 (1936).

(2) Pines and Ipatieff, THIS JOURNAL, **61**, 1076, 2728 (1939).

(3) Rosenbaum, Grosse and Jacobson, *ibid.*, **61**, 689 (1939).

(4) Reitz, *Z. physik. Chem.*, **B33**, 368 (1936).

1352(2, dp) (k, e), 1432(1d), (k, e), 1448(5d, dp) (k, e), 1470(2d) (k, e), 2868(8d, P) (p, k, i, e), 2906(5d) (q, p, k, e), 2960(9vvd) (q, p, k, i, e).

***t*-Amylcyclopentane.**—333(3) (k, i, ±e), 365(2) (k, ±e), 425(0d) (k, e), 443(0d) (k, e), 468(0d) (e), 477(0vd) (e), 513 (1) (k, e), 536(0) (k, e), 669(2) (k, e), 680(1) (k, e), 710(3b) (k, e), 750(0d) (e), 789(0d) (e), 852(1d) (k, e), 898(5b) (k, e), 932(2) (k, e), 953(0vd) (e), 972(0vd) (e), 1005(0) (e), 1017(1) (k, e), 1041(2) (k, e), 1049(2) (k, e), 1090(1) (k, e), 1129(0) (k, e), 1180(0) (k, e), 1209(0) (k, e), 1232(2b) (k, e), 1269(0) (k, e), 1293(0d) (k, e), 1319(0d) (k, e), 1338(0) (k, e), 1355(1) (k, e), 1446(8vd) (k, e), 1469(5vd) (k, e), 2717(0) (k, e), 2739(0d) (k, e), 2854(7) (q, k, e), 2868(8), (p, k, i, e), 2905(7d) (q, p, k, e), 2940(7d) (q, k, i, e), 2964 (10) (q, p, k, i, e).

3-Cyclopentylpentane.—330(4) (k, ±e), 345?(0vd) (e). 390(2b) (k, ±e), 427(0vd) (e), 444(0vd) (e), 488(0) (e), 535(1d) (e), 750(0d) (k, e), 775(0d) (k, e), 839(2vd) (k, e), 868(2b) (k, e), 898(6b) (k, e), 953(0vd) (k, e), 998(0) (k, e), 1016(0) (e), 1038(5b) (k, e), 1071(0) (k, e), 1089(0d) (k, e), 1131(1d) (k, e), 1153(0) (k, e), 1181(0d) (k, e), 1273(3) (k, e), 1309(0) (k, e), 1325(1) (k, e), 1353(1d) (k, e), 1371(0d) (k, e), 1445(8) (k, e), 1460(1) (k, e), 2729(0d) (k, e), 2844 (4) (k, e), 2869(10b) (p, k, i, e), 2901(2) (q, p, k, i, e), 2936 (10vd), (q, k, i, e), 2961(10) (q, p, k, i, e).

Discussion

The reading of these spectra was made very difficult by the extraordinary diffuseness of most of the lines, which accounts for the relatively poor agreement with previous work as shown in Table I. This diffuseness is in great contrast to the sharpness of the lines of benzene and cyclohexane (and their derivatives) and seems to indicate a real difference between these compounds and cyclopentane.[5]

TABLE I

CYCLOPENTANE

Reitz[a]	Weiler[b]	This paper
		207(0)
	231(00)	
285(1b)	292(0d)	288(1)
		712(0)
886(9)0.08	886(4)	888(10, P)
967(0)		
1028(4b)1.00	1031(1)	1032(4d, dp)
1102(1)0.90		
1216(1)1.00		
1283(2b)1.04		
		1298(1)
1446(4b)0.92	1450(2)	1448(5d, dp)
1479(1/2)dp		1482(1d)
2866(10)0.26	2870(4)	2869(10, P)
2898(4)	2905(1)	2901(4)
2941(12) } 0.36	2942(4d)	2943(7vd) } dp
2964(10) }	2973(1)	2970(6) }
	3868(d)	

METHYLCYCLOPENTANE

K., R. and S.[c]	This paper	K., R. and S.	This paper
218(1)	227(2)		1192(0d)
292(2)	314(1)	1204(2b)	
	344(2d)	1274(2)	1277(1d)
428(2)	430(1d)	1310(2b)	1318(1)
530(4)	534(4)	1348(1)	1352(3)
780(3b)			1427(2s)
	799(0vvd)	1452(6)	1453(6unsym)
842(5)	845(1vd)		1480(1d)
886(8)	894(6)	2722(4)	2728(1)
978(4)	980(1vd)	2865(12b)	2859(7d)
	999(0vvd)		2871(10)
1017(4)	1021(1d)		2912(2d)
1079(4)		2921(10b)	2928(9d)
	1131(0d)	2956(16b)	2961(9d)

[a] Reitz, *Z. physik. Chem.*, **33B**, 179 (1936); *ibid.* **38B**, 381 (1937). The numbers following Reitz' intensities are the values of the depolarization ratio ρ. [b] Weiler, *Z. Physik*, **69**, 586 (1931). [c] Reference 1.

The strong polarized line near 900 cm.$^{-1}$, arising from the "breathing" vibration of the cyclopentane ring, can be used to recognize cyclopentane derivatives in mixtures with other types of compounds. However, the minimum percentage which can be detected is relatively high because of the diffuseness mentioned above.

Summary

Raman spectra are described for cyclopentane and the following cyclopentane derivatives: methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *s*-butyl, *t*-butyl, *t*-amyl, and 3-cyclopentylpentane.

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(5) It is possible that this diffuseness may be evidence of a small deviation from planarity of the cyclopentane ring. The same conclusion, based on other evidence, is reached by Aston and co-workers, THIS JOURNAL, **63**, 2029 (1941).