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Raman and Infrared Spectra of 1,4-Dichloro-2-butyne

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In order to investigate whether a barrier to internal rotation in compounds $C(LMN)-C{\equiv}C-C(XYZ)$ is detectable by means of conventional Raman and infrared techniques, 1,4-dichloro-2-butyne was examined. The spectra show no signs of the presence of a barrier, but the existence of a *small* barrier (<100 cm^{-1}) cannot be excluded. For all 'practical' purposes the rotation may be considered as unhindered.

In the Vålådalmeeting (Sweden 1958) Pauling suggested that there might be a hindrance to the internal rotation about the bonds in compounds of the general formular $C(LMN)-C{\equiv}C-C(XYZ)$ and that the barrier might be as high as 0.5 kcal per mole ($\sim$ 175 cm^{-1}). In an earlier investigation by Thompson *et al.*[1] the barrier in $CH_3-C{\equiv}C-CH_3$ has been shown to be zero. The slight chance existed, however, that a larger barrier might be present in polar compounds like $CH_2Cl-C{\equiv}C-CH_2Cl$ (I). Electron-diffraction investigation of this compound has shown that the barrier is close to zero but admittedly this experimental procedure has no high sensitivity to fixation of the magnitude of small barriers. Of course, the experimental method *par excellence* to apply is a microwave investigation, either of (I) or, preferably, of a compound like $CH_3-C{\equiv}C-CH_2Cl$ (II) in which no rotational isomers would exist. This investigation has already been started by Laurie and Lide [3] who found that an upper limit to the height of a small barrier actually present in (II) is 0.1 kcal per mole ($\sim$ 35 cm^{-1}). — This result is in harmony with our recent studies of the infrared and Raman spectra of (I). If the barrier were *high* (1—3 kcal per mole), the usual signs of rotational isomerism such as "extra" lines would be expected. A *lower* barrier would have a chance to make itself noticed by its low-lying "pseudo"-torsional level(s). Nothing of this happens. In fact, the number of observed fundamentals is so small that the idea of a force-field of higher symmetry than the nuclear skeleton is hard to avoid. The observed spectra are interpretable in a straightforward manner — at least within the area of the usual medium-resolved infrared and Raman spectra — if one assumes unhindered rotation.

EXPERIMENTAL

$CH_2Cl-C\equiv C-CH_2Cl$ (I) was prepared[4] from 31 g of commercial $CH_2OH-C\equiv C-CH_2OH$. Yield 30 g (b. p. 49°—51°C at 75 mm Hg). By redistillation, 3 fractions were obtained which were identical with respect to their infrared absorption curves in the 600—4 000 cm^{-1} region. The Raman and the infrared spectra to be discussed refer to spectra of the middle fraction (20 g).

The *Raman spectrum* has earlier been photographed by Valette[5]. Our Raman spectrum, given in Table 1, is more complete than Valette's. Exposure periods of 2—6 h were applied. The quality of the high-dispersion spectrograph of high light-gathering power has been described elsewhere[6]. Line positions were measured against an iron-arc spectrum on photographic enlargements (1:15). They are thought to be reliable to 1—2 cm^{-1}.

Infrared spectra were recorded on a commercial Perkin-Elmer 21 instrument using KBr, NaCl, and CaF_2 optics in the appropriate regions. A cell thickness of 0.025 mm was applied except in regions where no or only very weak lines were found. Here, cells of 0.1 and even 1.0 mm thickness were used, except for the 400—650 cm^{-1} region where only one cell thickness was available (0.025 mm). The 'Optical D' given in Table 1 for reason of comparison, is the density that would have been found if the cell thickness 0.025 mm had been applied throughout. The frequencies measured in the infrared are thought to be good to 2—3 cm^{-1}.

INTERPRETATION OF SPECTRA

A glance at Table 1 shows that we are very far from observing the 24 fundamental vibrations to be expected for a molecule with 10 atoms. Most of the observed bands are obviously combination — and overtones. In view of the fact that a thorough Raman-infrared investigation usually brings out all or nearly all of the fundamentals[7], something exceptional is at work. We believe that this is the unhindered rotation, which causes a higher symmetry for the potential function than for the nuclear skeleton. Hence, a number of normal vibrations that would usually be observed separately, degenerate.

$CH_3-C\equiv C-CH_3$, with no barrier to the internal rotation, has the instantaneous symmetry D_3, but the symmetry of the potential field, and hence of the normal vibrations, is greater than this[8]. Actually the pseudo-symmetry of dimethylacetylene is D_{3d} (*not* D_{3h}). If this description can be extended to involve (I) the vibrations would be classified in four classes: A_{1g} (4 vibrations), A_{1u} (3), E_g (4 double-degenerate), and E_u (4 double-degenerate), *i.e.* 15 distinct normal frequencies. One might, however, suspect *a priori*, that the introduction of chlorine might cause changes analogous to what happens if, *e.g.*, one or more hydrogen atoms in a highly symmetrical hydrocarbon are substituted by deuterium. If all the symmetry elements are hereby removed, all 3N-6 normal vibrations are observed (thorough work provided). According to this latter description we should be able to find 24 fundamentals in the combined Raman and infrared spectra.

Before we counted the observed normal vibrations it seemed wise to investigate whether we were reasonably sure to have all of them recorded. For this purpose approximately correct modes of vibrations were constructed for (I) in the two extreme positions, *i.e.* the *trans* and the *cis* configuration where the symmetry is high enough (C_{2h} and C_{2v}) to make such sketching possible. It appeared that probably only one low-lying frequency might have escaped

Table 1. Observed Raman and infrared spectra of liquid $CH_2Cl-C\equiv C-CH_2Cl$ at 25°C.

Line No.	Raman spectrum		Infrared spectrum		Interpretation	
	Frequency	Intensity	Frequency	'Optical D'	Fundamental	Combination
0					$\nu_0 = 215$ cm^{-1}	(unobserved)
1	330*	2			$\nu_1 = 330$	
2	400–455 *	2			$\nu_2 = 425$	$2\nu_0 = 430$
3			435	0.2	$\nu_3 = 435$	
4			490	0.2	$\nu_4 = 490$	
5			545	0.03		$\nu_5 = \nu_0 + \nu_1 = 545$
6	700	10	700	10	$\nu_6 = 700$	$\nu_0 + \nu_4 = 705$
7			750	0.03		$\nu_7 = \nu_1 + \nu_2 = 755$
8			778	0.2	$\nu_8 = 778$	
9	785	8			$\nu_9 = 785$	
10	903	1	903	0.05	$\nu_{10} = 903$	$\nu_2 + \nu_4 = 915$
11			1 160	3	$\nu_{11} = 1\,160$	
12	1 165	2			$\nu_{12} = 1\,165$	
13			1 260	11	$\nu_{13} = 1\,260$	
14	1 266	10			$\nu_{14} = 1\,266$	
15			1 383	0.03		$\nu_{15} = \nu_0 + \nu_{12} = 1\,380$
16			1 425	1.1	$\nu_{16} = 1\,425$	
17	1 430	6			$\nu_{17} = 1\,430$	
18			1 602	0.02		$\nu_{18} = \nu_6 + \nu_{10} = 1\,603$
19			1 648	0.02		$\nu_{19} = \nu_0 + \nu_{17} = 1\,645$
20			1 653	0.02		$\nu_{20} = \nu_4 + \nu_{11} = 1\,650$
21			1 674	0.04		$\nu_{21} = \nu_8 + \nu_{10} = 1\,681$
22			1 750 *	0.01		$\nu_{22} = \nu_4 + \nu_{13} = 1\,750$
23			1 805	0.02		$\nu_{23} = 2\nu_{10} = 1\,806$
24			1 855	0.01		$\nu_{24} = \nu_2 + \nu_{17} = 1\,855$
25			1 944	0.01		$\nu_{25} = \nu_8 + \nu_{12} = 1\,943$
26			2 037	0.01		$\nu_{26} = \nu_8 + \nu_{13} = 2\,038$
27			2 067	0.01		$\nu_{27} = \nu_{10} + \nu_{12} = 2\,068$
28			2 115	0.01		$\nu_{28} = \nu_6 + \nu_{16} = 2\,125$
29			2 160	0.01		$\nu_{29} = \nu_{10} + \nu_{13} = 2\,163$
30			2 195	0.01		$\nu_{30} = \nu_8 + \nu_{16} = 2\,203$
31			2 232	0.02		$\nu_{31} = \nu_9 + \nu_{17} = 2\,215$
32	2 245	10			$\nu_{32} = 2\,245$	
33			2 312	0.10		$\nu_{33} = 2\nu_{11} = 2\,320$
34			2 325	v.w.		$\nu_{34} = \nu_{11} + \nu_{12} = 2\,325$
35	2 331	4				$\nu_{35} = 2\nu_{12} = 2\,330$
36			2 417	0.02		$\nu_{36} = \nu_{11} + \nu_{13} = 2\,420$
37	2 423	0				$\nu_{37} = \nu_{12} + \nu_{13} = 2\,425$
38	2 505	0				$\nu_{38} = 2\nu_{14} = 2\,532$
39			2 510	0.01		$\nu_{39} = 2\nu_{13} = 2\,520$
40			2 585	0.01		$\nu_{40} = \nu_{16} + \nu_{11} = 2\,585$
41			2 831	0.05		$\nu_{41} = 2\nu_{16} = 2\,850$
42			2 947	0.35	$\nu_{42} = 2\,947$	$\nu_6 + \nu_{32} = 2\,945$
45	2 954	10			$\nu_{43} = 2\,954$	
44			2 990	0.45	$\nu_{44} = 2\,990$	
45	2 995	3			$\nu_{45} = 2\,995$	

* Broad band.

observation in harmony with the findings of Crawford[9] for $CH_3-C\equiv C-CH_3$, in the spectrum of which a low-lying level at 213 cm^{-1} was found. If we assume that we did not observe a band at 215 cm^{-1} (*outside* the region accessible to us in the infrared and *in* a region where our Raman spectrum has some background) our scheme of combination bands fits well.

Table 1, then, indicates that we have observed fundamentals at 330, 425, 435, 490, 700, 778, 785, 903, 1 160, 1 165, 1 260, 1 266, 1 425, 1 430, 2 245, 2 947, 2 954, 2 990 and 2 995 cm^{-1}, *i.e.* 19 fundamentals. However, some of the observed bands may be grouped in close pairs, *viz.* 425—435, 778—785, 1 160—1 165, 1 260—1 266, 1 425—1 430. Counting "pairs + singles" we get 14 (+ 1 unobserved = 15). Thus, a description of the molecule as freely rotating but very slightly perturbed due to the chlorines, seems rather adequate.

For the present purpose we shall refrain from giving the forms of the normal vibrations although they are rather obvious in some of the cases (C—Cl valence vibrations at 700 and 778, C—C at 903 and 1 160, CH_2 scissoring at 1 425, C≡C vibration at 2 245 and C—H vibrations at 2 947, 2 954, 2 990 and 2 995). The numbering of the frequencies in Table 1 is completely arbitrary.

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