

Homework 5 (IR Spectroscopy)  
Selected answers  
C343

Additional Problems:

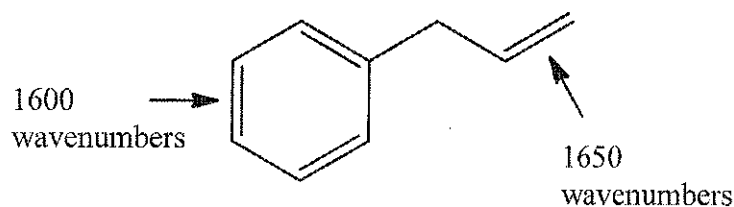
1. Why are some IR signals very intense and some IR signals don't show up at all?

Intensity is proportional to dipole moment—a stretch with a strong dipole absorbs IR light well, leading to a large signal. This is why carbonyl and nitrile stretches are relatively strong, while many C=C stretches are weak, or don't show up at all if symmetrical.

2. Why is IR a good technique for determining which functional groups are present in a molecule?

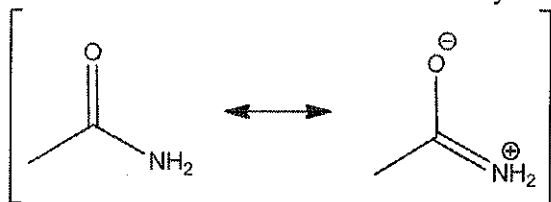
IR can be used to determine the presence or absence of bonds based on mass of atoms attached and bond strength—in other words, it is good at characterizing bonds. Since functional groups are defined by their unique group of bonds, IR is excellent at characterization of functional groups.

3. What IR frequencies would be expected for the C=C bonds indicated? Why do they absorb light of different frequencies?



The benzene pi bond is in a conjugated system, and therefore has more single bond character, lowering its stretching frequency.

4. Give a physical explanation of why the carbonyls of amides absorb at lower wavenumber than other carbonyls.

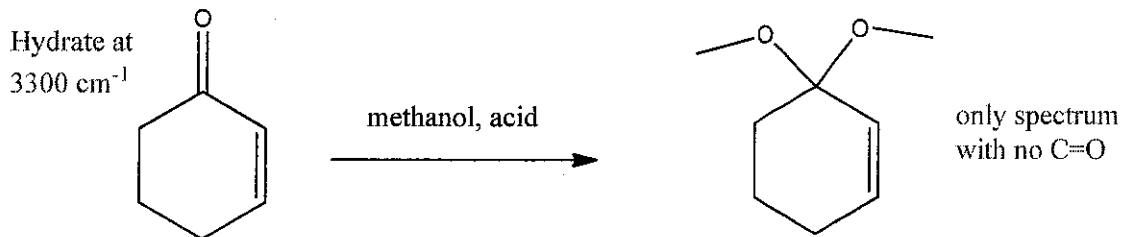


The amide has an exceptionally stable (and therefore significant) contributor to the single bond character of the carbonyl, making it have a lower stretching frequency.

5. How would you use IR to distinguish between a compound containing an aldehyde and a compound containing a ketone?

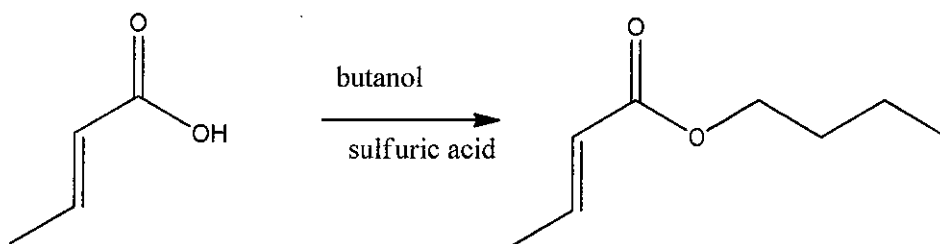
Both have a carbonyl stretch at about  $1710\text{ cm}^{-1}$ , but the aldehyde also has a C-H stretch at  $2700/2800\text{ cm}^{-1}$ .

6.



Spectrum letter:   B  

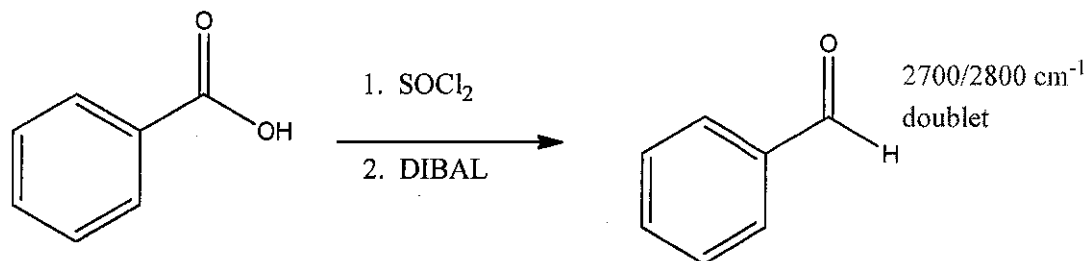
Spectrum letter:   E  



Spectrum letter:   F  

Spectrum letter:   A  

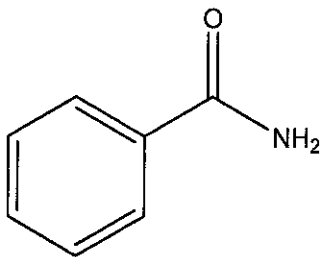
F and D similar except C=C stretch at  $1600\text{ vs }1650\text{ cm}^{-1}$



Spectrum letter:   D  

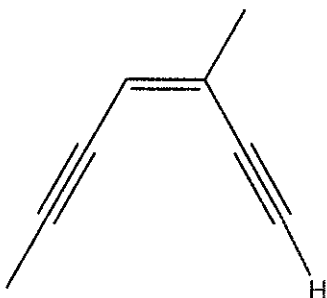
Spectrum letter:   C

7. What characteristic peaks would you expect to observe on an IR spectrum of this molecule? Give expected frequencies, and indicate the one that would be expected to be most intense.



Expect to see an intense carbonyl peak. Typically, this amide would be at  $1650\text{ cm}^{-1}$ , but conjugation lowers it by  $25\text{ cm}^{-1}$  to  $1625\text{ cm}^{-1}$ . Other characteristic peaks are C=C aromatic at  $1600\text{ cm}^{-1}$ , NH doublet (symmetric and asymmetric) around  $3300\text{ cm}^{-1}$ , and C-H stretches above  $3000\text{ cm}^{-1}$  because all carbons are  $sp^2$  hybridized.

8. Which C-H bond in the molecule below would have the highest frequency stretch? Give an explanation based on physical principles.



The alkyne C-H stretch is highest frequency because it is the strongest bond. It has the most s-character in the sigma bond because it is the overlap of an s orbital with an  $sp$  hybridized orbital.

9. Compare the carbon/carbon triple bond to the carbon/nitrogen triple bond.

A. If you took into account only the atomic mass, you would expect the  $C\equiv N$  to have a lower frequency than the  $C\equiv C$  triple bond, but this isn't true. Explain why the opposite is true.

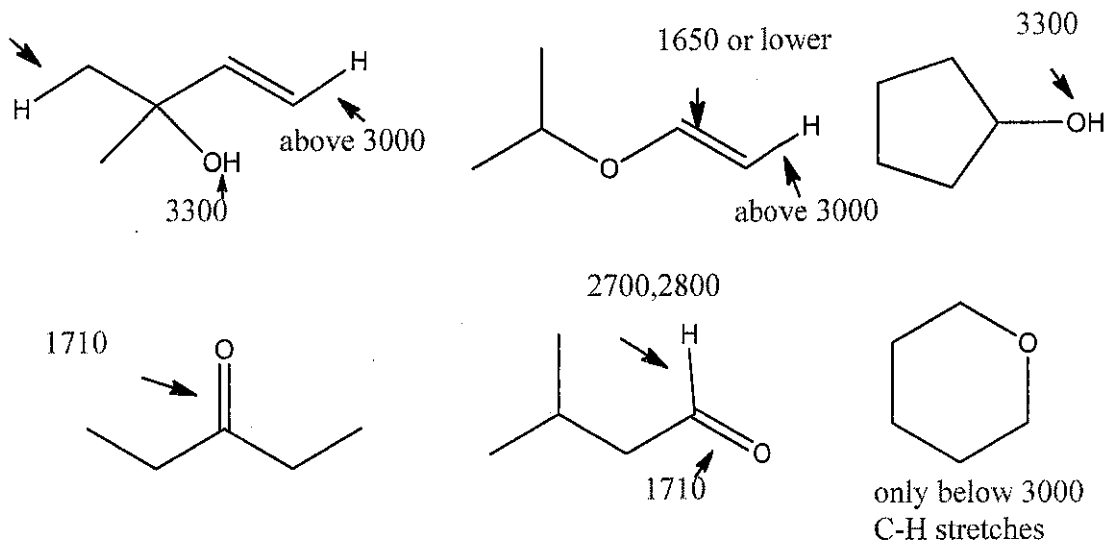
Once must also consider the bond strength. The  $C/N$  triple bond is much stronger due to electrostatic interaction, and this factor is evidently more important than the slight mass difference between carbon and nitrogen.

B. Which stretch,  $C\equiv C$  or  $C\equiv N$ , is more intense? Why?

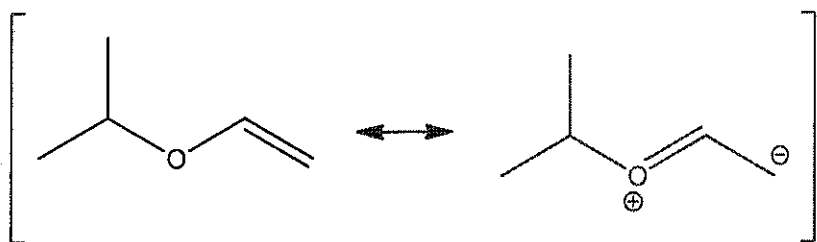
$C\equiv N$  is more intense because intensity depends on the dipole, and this is a more polar bond.

10. List the characteristic IR frequencies for these C<sub>5</sub>H<sub>10</sub>O compounds.

All numbers below are in units of wavenumber (cm<sup>-1</sup>). All compounds contain below 3000 cm<sup>-1</sup> C-H stretches.



11. The C=C stretch of isopropyl vinyl ether is unusually intense. Why?



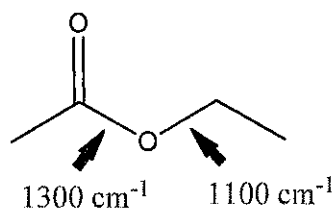
Resonance shows that this bond is highly polar, with a positive and negative end.

12. Which stretching frequencies will be similar between these two compounds? Which will be distinct?

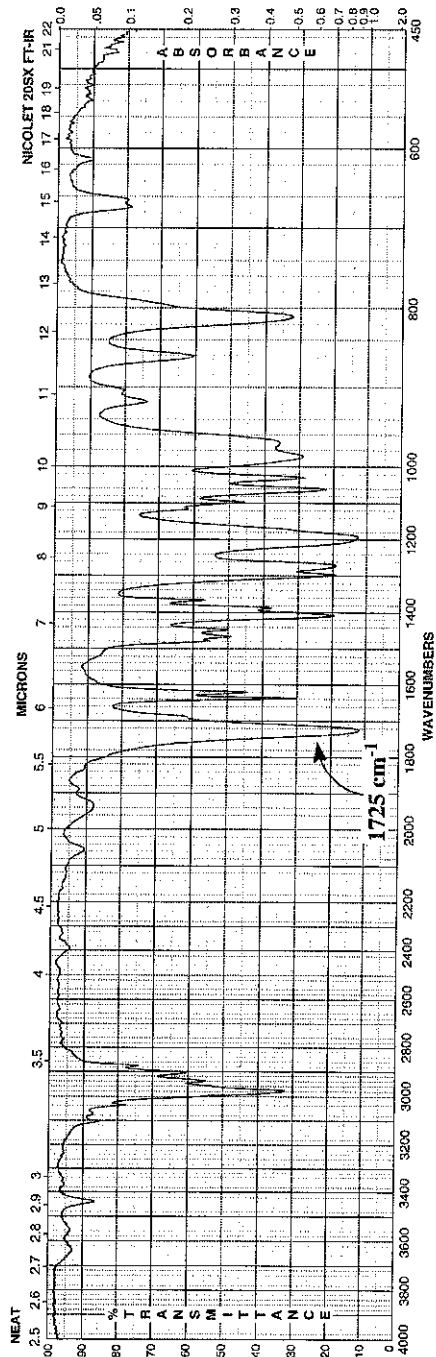
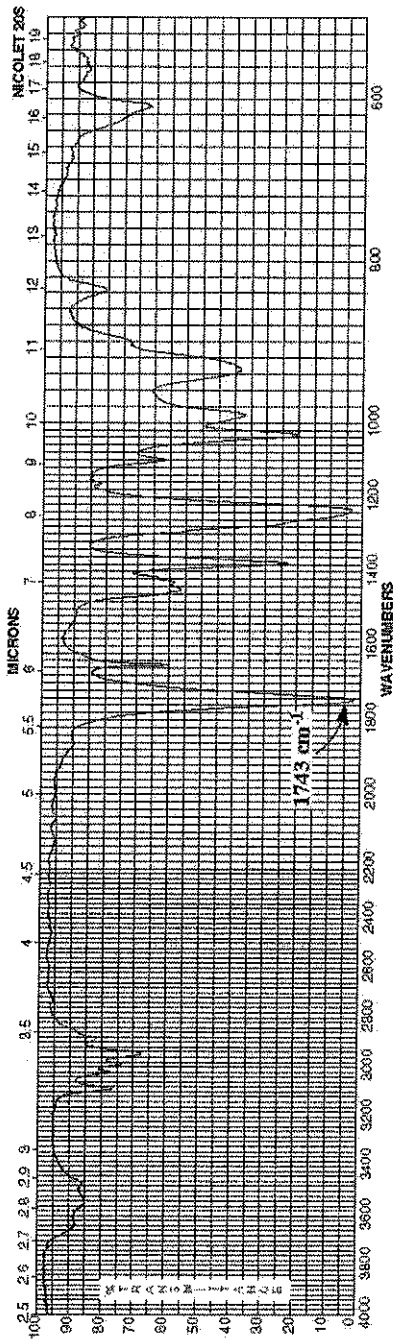
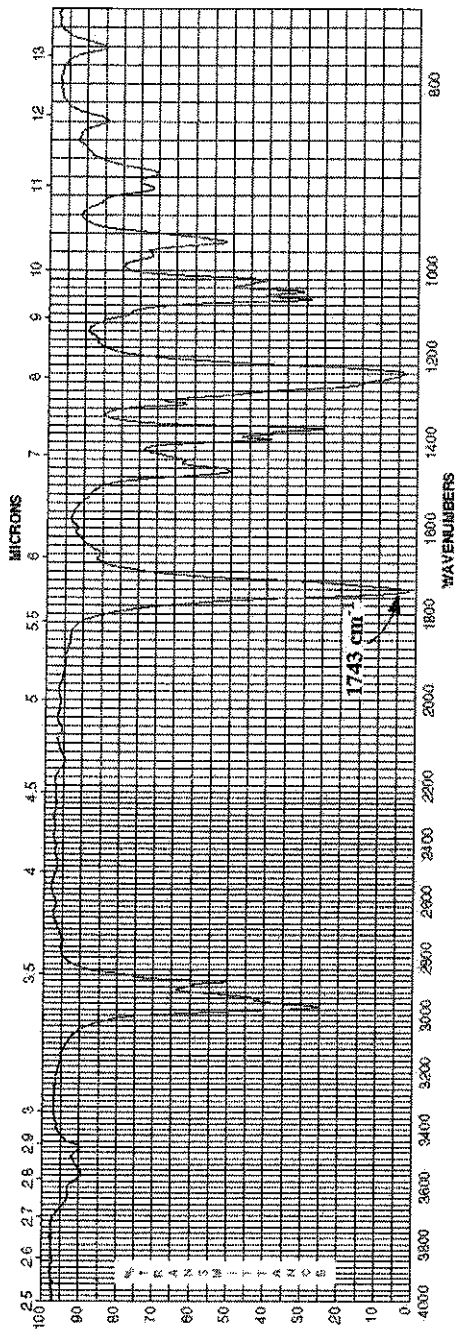
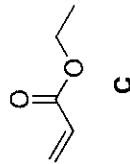
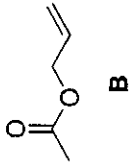
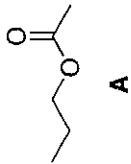


The carbonyl stretches of a ketone and a conjugated ester are both around 1685 cm<sup>-1</sup>, and both have CH stretches above and below 3000 cm<sup>-1</sup>. The only distinguishing stretch is C=C, which is about 1650 cm<sup>-1</sup> on the left and 1625 cm<sup>-1</sup> (or so) on the right.

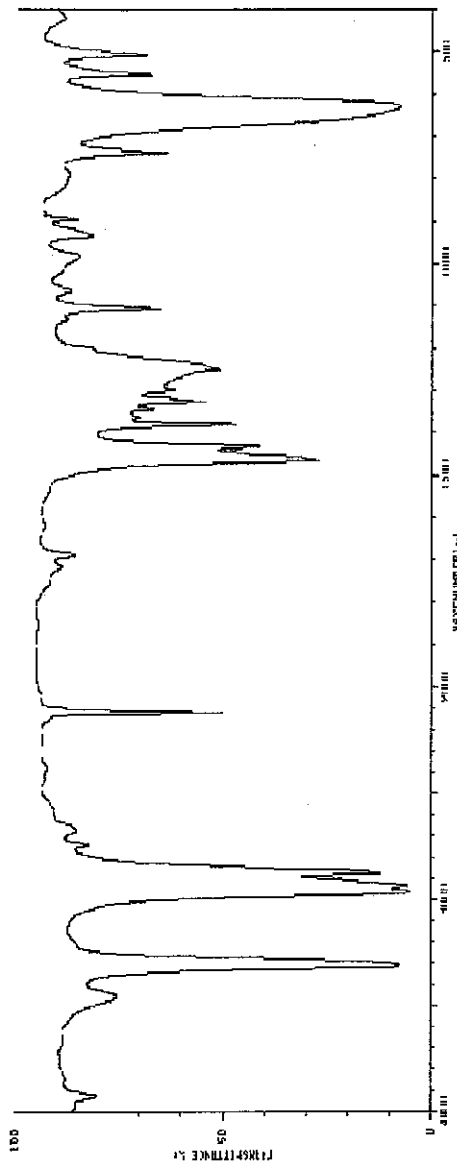
13. An ester has two distinct C-O bonds. Explain why one has a stretching frequency of 1300 wavenumbers and one has a frequency of about 1100 wavenumbers. (Use both resonance and induction arguments.)



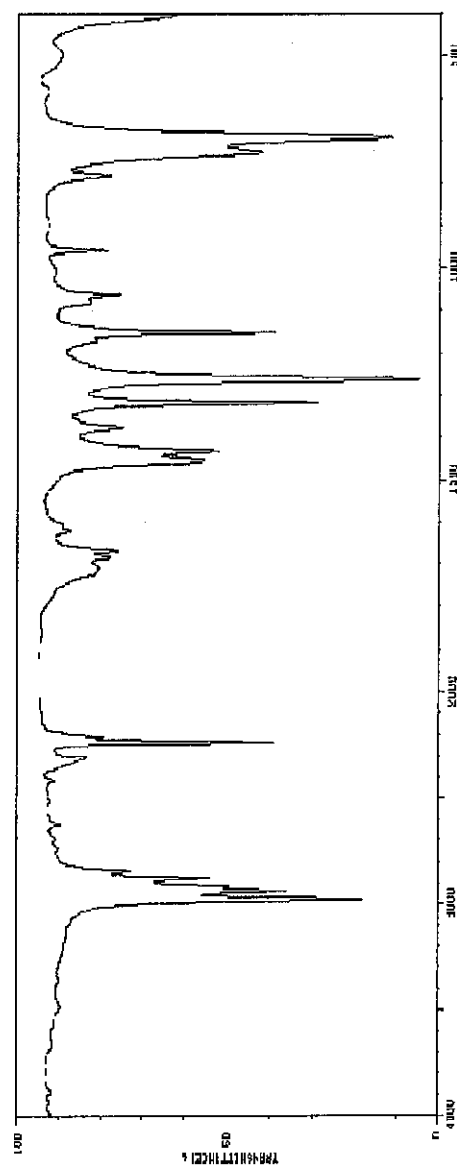
The left C-O bond is stronger. This can be argued from resonance, because there is a contributor that gives this bond double bond character. It can be argued by induction—the carbonyl makes the carbon partially positive, so it tightens the C-O bond. Or argue that the carbonyl carbon atom is  $sp^2$  hybridized, so it has a shorter bond (also being more electronegative.)



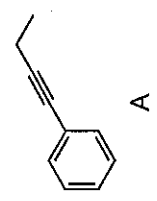
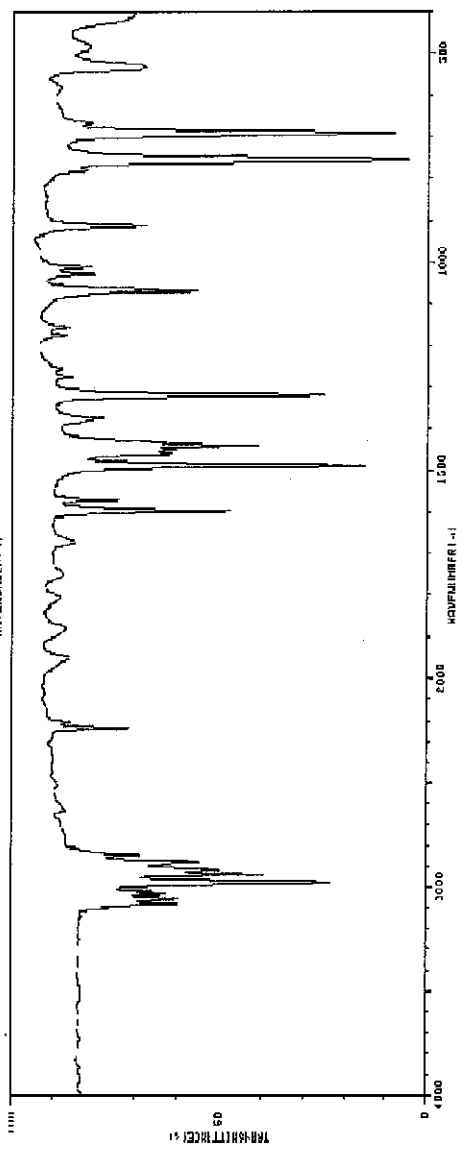
15



3926	77	2678	81	1432	39	1250	49	740	60
3455	72	2120	49	1380	46	1107	62	730	72
3111	7	2097	84	1366	88	1063	84	630	7
2962	4	1717	85	1344	84	983	81	555	64
2937	5	1690	81	1328	52	934	79	509	66
2876	11	1467	25	1320	58	895	81		
2738	79	1461	29	1300	68	793	84		



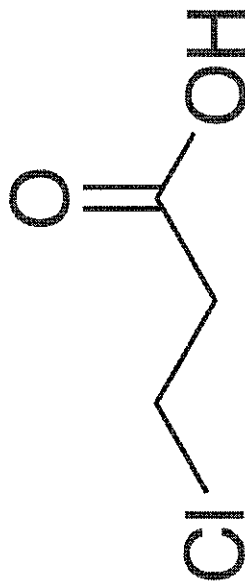
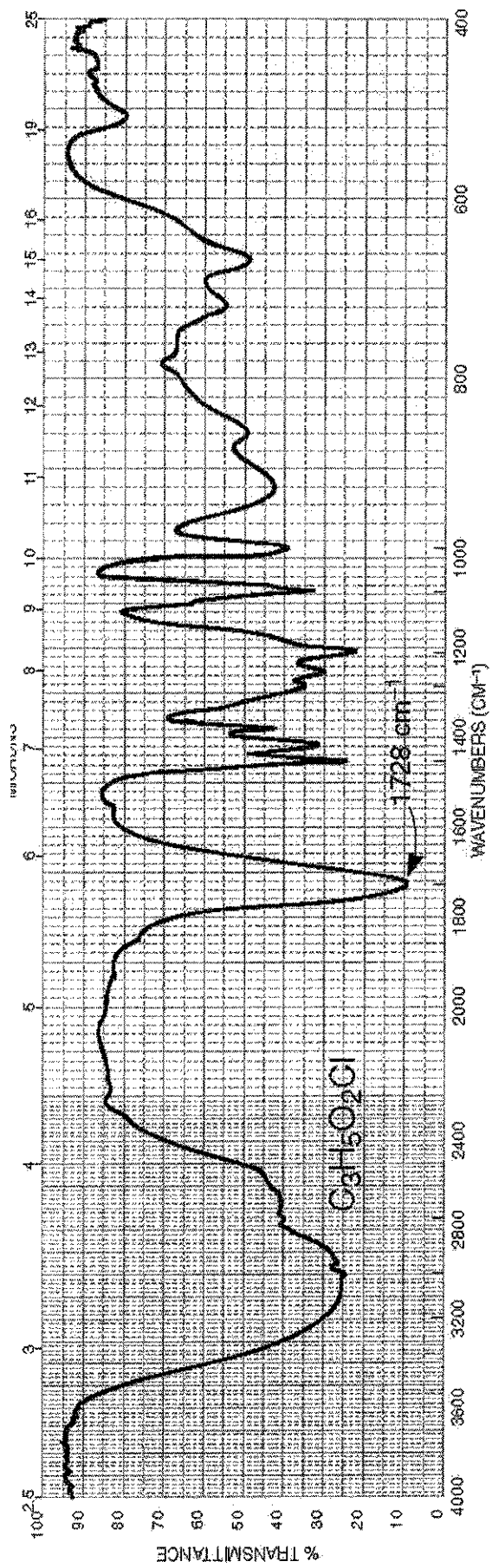
2981	17	2241	37	1607	85	1080	79	494	86
2941	35	2214	77	1455	53	1075	79		
2922	47	1708	77	1434	50	1063	72		
2880	62	1689	74	1378	72	968	77		
2847	70	1668	74	1320	27	782	74		
2825	86	1622	84	1264	4	727	41		
2308	79	1612	86	1154	37	692	11		



3101	72	2917	47	1699	46	1376	74	766	4
3081	58	2878	52	1573	72	1321	24	692	7
3055	58	2845	65	1492	14	1070	59	668	79
3034	60	2809	81	1452	68	1030	77	639	66
3021	64	2237	70	1452	58	1012	79	533	66
2978	22	2208	81	1442	39	914	66	522	72
2939	38	1673	81	1434	60	781	78	485	79



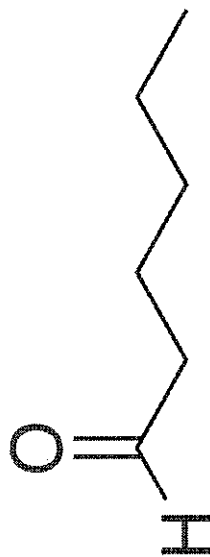
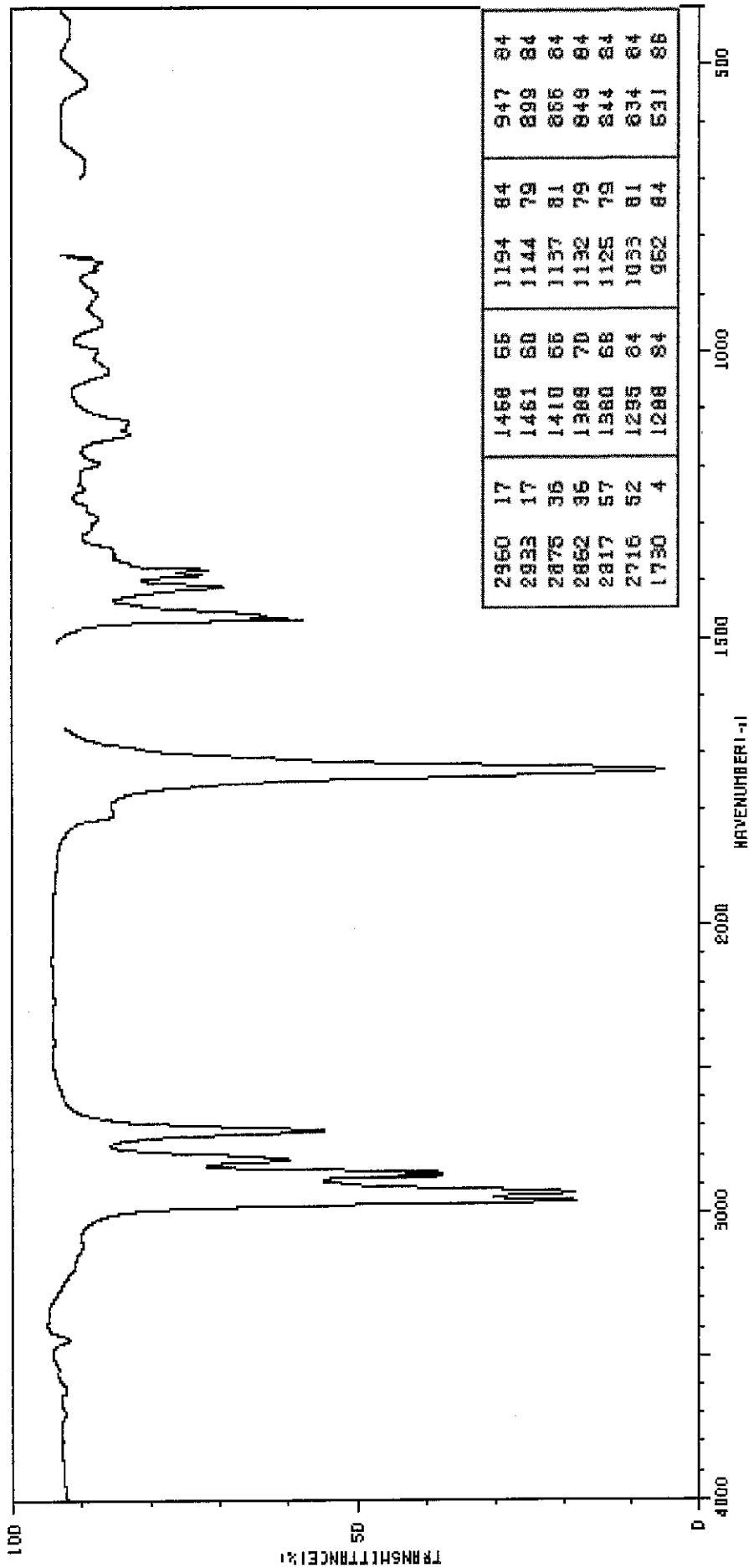
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17

M = 100



$C_5H_{10}N_2$  (weak signals above 3100 are 'junk')

18

