CENTER OF MASS DISPLACEMENT AND RELAXATION TIMES OF LINEAR ALKYNES

J. M. BERNASSAU, M. BERTRANNE, C. COLLONGUES et M. FETIZON

Laboratoire de Synthèse Organique, Ecole Polytechnique 91128 Palaiseau, Cedex, France

(Received in France 12 June 1984)

Abstract - The carbon-13 chemical shifts and relaxation times of various linear alkynes have been measured . Complexation of these compounds with dicobalt octacarbonyl induces changes in δ 's and T_1 's . Unambiguous assignments were obtained from deuterium labelled octynes . The T_1 variations result from the displacement of the center of mass of the aliphatic chain . They are systematic and can thus be used for assignment purposes .

The dynamic information obtainable from carbon-13 relaxation time measurements allows to probe into the short time behaviour of individual atoms of molecules in solution . When internal motions are present, it is possible to follow the relative variations in mobility associated with these processes . This is the case of long chain aliphatic compounds and indeed such studies have been conducted on a large variety of substances including visual chromophores such as retinal¹, prostaglandins², surfactants³, fatty acids⁴ and other long-chain molecules^{5,6}. Theory⁷⁻¹⁰ supports the intuitive feeling that if an extremity of the chain is held either by inertial or intermolecular forces, motion and T₁ increase towards the opposite end . In the first case the center of mass is defined by a heavy atom of molecular backbone . In the second case, one chain termination is loosely "anchored" in the surrounding medium by hydrogen bonding . This kind of effect can easily be demonstrated in long chain carboxylic acids or esters⁴. The former compounds display carbon-13 T₁ increase from the COOH group to the other end, whereas in the latter compounds the T₁ increase from the center of the aliphatic chain to its extremities.

Although it is rather easy to introduce or remove an hydrogen bond between solvent and molecule^{4,11} and study the variation in longitudinal relaxation time thus induced, it is generally more difficult to move the molecular center of mass in order to perform similar studies. The molecules choosen in the present work allow one to conveniently switch their center of mass from a central to a terminal position by complexation with a transition metal. Such complexation introduces chemical shifts and relaxation times changes which are both very predictable and can thus be used for assignment purposes .

The paper is divided in two parts . The first part describes the synthesis of some labelled compounds which were necessary to allow unambiguous chemical shift assignments . The second part analyses the δ and T_1 changes upon complexation of the terminal triple bond with dicobalt octacarbonyl .

SYNTHESIS OF OCTYNE-1 LABELLED IN POSITION 3,3 ; 4,4 ; 5,5 or 6,6

In order to establish without ambiguity the effect of cobalt complexation upon the carbon chemical shifts, four labelled compounds were synthesized according to the general synthetic scheme of Figure 1.

I - SYNTHESIS OF d2 3,3 ; 4,4 ; 5,5 or 6,6 OCTYNES (8a to 8b)

Synthesis proceeds from hexanols doubly deuterated in position 1 through 4 . Each of these compounds is then brominated and a triple bond is added leading to the corresponding octypes.



- 1°/ deuterated hexanols <u>6a</u>, <u>6b</u>, <u>6c</u>, <u>6d</u>
- a/ $\underline{6a}$ is directly obtained by reducting caproic acid ethyl ester with $LiAlD_4$.
- b/ in the same manner propyl, butyl and pentyl esters yield the corresponding deuterated alcohols. In each case the bromide is then prepared by action of $HBr-H_2SO_4$ ¹².
- c/ through an appropriate Grignard reaction d_2 -1,1 bromopropane, butane and pentane respectively provide <u>6d</u>, <u>6c</u> and <u>6b</u>:
- d_2 -1,1 propyl magnesium bromide <u>1</u> is allowed to react with allyl bromide¹³ giving hexene d_2 -4,4 <u>2</u> which is hydroborated leading to d_2 -4,4 hexanol <u>6d</u>.
- d_2 -1,1 butyl magnesium bromide 3 and ethylene oxide furnish d_2 -3,3 hexanol $\underline{6c}^{14}$.
- d_2 -1,1 pentyl magnesium bromide $\underline{4}$ and carbon dioxide yield d_2 -2,2 hexanoic acid $\underline{5}^{15}$.

Reduction with LiAlH₄ affords d_2 -2,2 hexanol <u>6b</u>.

2°/ octynes

Each of the preceding hexanols is then converted to the bromides $\underline{7}$ by action of HBr-H₂SO₄. By reaction of these compounds with lithium acetylenide-ethylenediamine complex, octynes 8<u>a</u>, 8<u>b</u>, 8<u>c</u>, 8<u>d</u> are obtained in good yield¹⁶.

3°/ octynes dicobalt hexacarbonyl complexes $\underline{8a}^{"}$ to $\underline{8b}^{"}$

It has been reported that the two bridge carbonyl groups of dicobalt octacarbonyl can be replaced by $alkynes^{17}$. The I.R. spectra of the alkyne complexes are so characteristic that they can be used to ascertain the nature of the final compound.

CARBON CHEMICAL SHIFTS

The carbon chemical shift assignments of the uncomplexed alkynes present little difficulty. Table I summarizes the data for the compounds used in this work : pentyne 9, hexyne 10, heptyne 11, octyne 8, decyne 12, dodecyne 13, cyclododecyne 14, octyne-1 ol-3 15 and octyne-2-oic methyl-ester 16. All the deuterated compounds exhibit the expected upfield chemical shift changes relative to the hydrogenated compounds : 0.6 ppm for the carbon bearing the deuterons and 0.2 ppm for the neighbouring carbons.

These chemical shifts are similar to those already published $^{18-23}$. Some differences occur however, reaching up to 2 ppm. Their systematic nature indicates that they are the result of different experimental conditions (solvent, reference). In no case are our assignments in conflict with those already reported.

Upon reacting these substances with an equimolar amount of dicobalt octacarbonyl, dicobalt complexes of the terminal triple bond are formed¹⁷ inducing serious changes in the chemical shifts. From the spectra of the labelled compounds, the assignments of the resonances of the cobalt complexes are straightforward.

The effect of cobalt complexation upon the carbon-13 chemical of compounds $\underline{8a}$ to $\underline{8d}$ follows a systematic pattern. The two carbons forming the triple bond undergo downfield shifts of + 5 and + 13 ppm, the methine being the less affected. The largest induced shift occurs for

compound s	carbon N°	1	2	3	4	5	6	7	8	9	10	11	12
pentyne - 1	<u>9</u>	68.0	84.3	20.2	21.7	13.2							
hexyne - 1	<u>10</u>	67.9	84.5	17.9	30.3	21.7	13.4						
heptyne-1	<u>11</u>	67.9	84.5	18.2	28.0	30.8	22.0	13.8					
octyne-1	<u>8</u>	67.9	84.6	18.3	28.3	28.3	31.2	22.4	13.9				
decyne - 1	<u>12</u>	67.9	84.6	18.3	28.4	28.6	28.9	29.0	31.7	22.5	13.9		
dodecyne - 1	<u>13</u>	67.8	84.5	18.2	28.3	28.6	28.9	29.4	29.4	29.2	31.7	22.5	13.9
cyclododecy	me <u>14</u>	81.5	81.5	18.3	25.5 ^b	25.4 ⁶	24.7 ^b	24.4 ^b	24.4 ^b	24.7 ⁶	25.4 ⁶	25.5 ⁶	18.3
octyne-1 ol	-3 <u>15</u>	72.5	84.8	61.6	37.2	24.4	31.1	22.2	13.6				
methy1 octynoate	<u>16</u>	89.4	72.4	18.1	26.8	30.5	21.7	13.5					

Table I - Carbon-13 chemical shifts ^[2] of selected compounds

a) δ values in parts per million downfield from Me₄Si ; δ (Me₄Si) = δ (CDCl₇) + 76.9 ppm

b) Assignments may be interchanged

the carbon α to the triple bond where it reaches a value of + 15 ppm . This is in accordance with the dissapearance of the triple bond upon cobalt complexation, since carbon α to an alkynic linkage usually exhibit a 15 ppm upfield displacement with respect to the corresponding alkenes .

Further away from the triple bond the change in chemical shift rapidly decreases past the β position where its value is + 3.4 ppm. Upon complexation with dicobalt octacarbonyl all the resonances of the carbons close to the complexing site therefore move downfield.

LONGITUDINAL RELAXATION TIMES

The longitudinal relaxation times were then measured . Table II lists the values obtained after the 3 parameter exponential fit for both uncomplexed and complexed compounds . The errors affecting the T_1 values are typically 5 %, reaching 10 % in some cases . More importantly, this error is in most cases smaller than the difference between T_1 values belonging to a particular compound . Since the T_1 values will be discussed in term of dipolar relaxation, the proton carbon Nuclear Overhauser Effect was measured by the gated decoupling experiment . The enhancement was found to be 2.8 \pm 0.1 on all the hydrogen bearing carbon resonances, thus ascertaining the dipolar nature of the relaxation .

For dipole-dipole relaxation the carbon relaxation time is directly related to the mobility of the C-H bonds issued from the carbon under consideration . In the long chain compounds this mobility has been shown to increase along the chain as a consequence of internal motion around the C-C bonds . In the absence of intermolecular forces which would restrain the reorientation process at some specific locations in the chain the mobility and thus T_1 increase monoto-

compounds (b)	carbon N°	3	4	5	6	7	8	9	10	11	12
pentyne-1	<u>9</u>	13.6	11.6	9.8							
	<u>9</u> "	2.1	2.3	2.6							
hexyne-1	<u>10</u>	9,2	8.5	9.2	7.0						
	<u>10</u> "	1.8	2.0	2.3	2.6						
hontime 1	<u>11</u>	6.6	6.4	6.8	7.2	6.1					
nepcyne- (<u>11</u> "	1.5	1.8	2.2	2.7	3.0					
	8	6.4	6.4	6.4	6.1	7.7	6.7				
octyne -1	<u>8</u> "	1.3	1.5	1.8	2.3	2.7	3.2				
docume t	<u>12</u>	4.4	4.2	4.2	4.2	4.1	5.4	5.8	5.5		
decyne - I	<u>12</u> "	1.3	1.4	1.7 ^e	2.1 ⁰	2.10	2.7	3.7	4.4		
dedemme 1	<u>13</u>	3.7	3.3	3.1	3.1	3.1	3.1	3.2	4.3	5.0	5.1
dodecyne - f	<u>13</u> *	1.2	1.5	1.7	1.7	1.7	1.9	1.9	2.8	4.0	4.4
	14	3.7	3.3	3.2	3.3	3.5	3.5	3.3	3.2	3.3	3.7
dodecyne	<u>14</u> ²²	1.0	1.0	1.2 ^C	1.1 ^c	1.19	1.1 ^c	1.1 ^c	1.2 ^c	1.0	1.0
octyne-1	<u>15</u>	1.9	1.0	1.3	1.9	2.4	3.0				
01-3	<u>15</u> *	1.3	0.8	1.1	1.5	2.0	2.6				
methyl octynoate	<u>16</u>		2.7	2.5	3.0	3.7	3.9				
	16 ^{°°}		0.8	1.2	1.5	2.1	2.4				

Table II - T_1 of uncomplexed and complexed compounds ^(a)

a) Values in seconds

b) A Star denotes the dicobalt complex

c) The Assignments may be interchanged

nically from the center of the molecule to its extremities . As can be seen from Table II this is the case for compounds 8 to 13 . For these compounds the center of mass can be loosely defined to be at the center of the aliphatic chain .

Upon complexation with dicobalt octacarbonyl the center of mass of the molecule is now displaced toward the triple bond . In fact since the added weight due to the Co $(00)_6$ group is close to 300 it can be safely assumed that the center of mass is very close to the triple bond . In the absence of intermolecular forces, mobility is thus only the result of the segmental motion of the carbon chain and the T_1 's are therefore found in increasing order from the double bond to the opposite extremity . It is worth noting that this effect extends much further away than the chemical effects due to the cobalt complex, which was, as generally noted for through bond effects limited to c.a. 4 carbon-carbon bonds .

The motional effects are of course only effective when segmental motion is $\ensuremath{\mathsf{present}}^{7-10}$. As a counter example, cyclododecyne 14 and its complex $14^{"}$ do not possess this property and the effect of cobalt complexation results only in a overall shortening of the T_1 values due to the increased molecular size .

When polar groups are present and if they are not prone to intermolecular hydrogen bonds the situation is unchanged. This is the case of 16 which upon cobalt complexation possesses carbon T_1 's ordered from the triple bond to the other end . In the presence of hydrogen bonding group the situation may change drastically, except if, as in 15, the polar group is close to the double bond . In this particular case, both inertial and intermolecular forces cooperate to the ordering of the relaxation times .

CONCLUSION

The present study demonstrates rather vividly the effects that can be expected from inertial effects in long chain molecules . Whereas in the absence of an heavy mass along the chain the longitudinal relaxation times increase from the center of the chain to its extremity, introduction af an heavy mass at one end of the chain results in monotonically increasing T_1 's from the site of introduction to the other extremity . The reliability and reproductivity of these effects allow them to be used as assignments aids . As such their range extends further away than usual chemical shift effects and may prove to be operative when other methods fail .

EXPERIMENTAL

The carbon spectra were recorded at 25 MHz on a VARIAN XL.100, using internal deuterium lock (CDC1₃). The concentration of the samples was c.a. 1 M . All spectra used 32 K points, the f.i.d.'s being zero filled if necessary . The T_1 values were obtained by the inversion recovery technique (24), 90 pulse width was 16 µsec. 8 to 11 values of τ were choosen in the appropriate range and the data fitted with a 3 parameter exponential curve. Standard errors were always less than 10 % and typically better than 5 %.

The solution of cobalt complexes in $CDC1_3$ were centrifugated before used .

I - d_2 -4,4 hexanol <u>6d</u>

$1^{\circ}/d_{2}-4,4$ hexene 2

A Grignard reagent is prepared from 2 g of magnesium and 8.8 g of d_2 -1,1 propyl bromide 1 in 20 ml of anhydrous ether. This reagent is transfered and filtered under pressure, using dried nitrogen, in another flask .

9.7 g of allyl bromide are added dropwise during 45 minutes. The reaction mixture is refluxed for a quarter of an hour before being hydrolysed with ice and ammonium chloride solution. The ethereal solution is dried over calcium chloride and distilled . A mixture of hexene in dry ether is collected and used as such in the following step .

2°/ 6d To the precedent mixture diluted with 20 ml of dried T.H.F. are added slowly 35 ml of a 1M T.H.F. diborane solution . The flask is kept for one hour at room temperature .

The excess hydride is carefully decomposed by 2 ml of water . The organoborane is oxidized at 30°-50°C by addition of 17 ml of 3M sodium hydroxide, followed by the dropwise addition of 17 ml of 30 % hydrogen peroxide . After one hour the reaction mixture is saturated with potassium carbonate. The organic layer is separated, the aqueous phase extracted twice with 30 ml of ether. The organic combined phases are dried, the solvent removed and $\underline{6d}$ (2.1 g) is distilled (Eb. = 148°). Yield is 29 % from <u>1</u>.

Eb. : 148°/760 mm I.R. (film) : 3350 - 2100 - 2180 N.M.R. 13C : 62.4 ; 32.3 ; 25.0 ; 22.2 ; 13.8 .

II - d₂-3,3 hexanol <u>6c</u>

A Grignard reagent is prepared from 5.4 g of d_2 -1,1 butyl bromide 3 and 1 g of magnesium in 20 ml of dry ether .

2 ml of condensed ethylene oxide (0°) are allowed to bubble into the reaction flask. After two hours, the viscous final mixture is diluted with 20 ml of ether and hydrolysed with ice . 30 % sulfuric acid is added until all the magnesium hydroxide is dissolved . The ethereal layer is refluxed for one hour with 20 ml of 20 % sodium hydroxide, washed once with a phosphate buffer $(KH_2PO_4 0.025M, Na_2HPO_4 0.025M, pH : 7)$.

Distillation affords 2 g of 6c $(R = 50 \)$. Eb. : 150°/760 mm I.R. (film) : 3350 - 2100 - 2180 N.M.R. 13C : 62.3 ; 32.1 ; 31.2 ; 22.4 ; 13.8 .

III - d₂-2,2 hexanol <u>6b</u>

1°/ d_2 -2,2 hexanoic acid <u>5</u>

A Grignard reagent is prepared from 6 g of d_2 -1,1 pentyl bromide $\frac{4}{2}$ and 1 g of magnesium in 20 ml of anhydrous ether .

The reaction mixture is poured into 60 g of dry ice in 280 ml of anhydrous ether and hydrolysed with 10 ml of 25 % sulfuric acid .

The ethereal layer is washed twice with 100 ml of 25 % sodium hydroxide . The alkaline extract is boiled to remove ether and volatile impurities. It is then acidified with concentrated hydrochloric acid until no more acid layer separated . 2.4 g of crude product are obtained (R = 52) dried over sodium sulfate and distilled (Eb. = 200°/760 mm).

 2° / <u>6b</u> To a solution of 900 mg of lithium aluminium hydride in 20 ml of dry ether are added 2 g of 5 in 20 ml of dry ether. The mixture is refluxed for one hour. Usual work-up affords 2 g of crude product . Distillation yields 1.6 g of $\underline{6b}$. Eb. : 151°/760 mm I.R. (film) : 3350 - 2100 - 2180 N.M.R. 13C : 62.2 ; 31.4 ; 25.0 ; 22.4 ; 13.8 .

IV - d_2 -1,1 hexanol <u>6a</u>

To a suspension of 3 g of LiAlD₄ in 100 ml of dry ether are added slowly 5 g of ethyl caproate in 30 ml of dry ether. The reaction mixture is refluxed for one hour. Usual work-up and distillation of the crude product afford 3.2 g of $\underline{6a}$ (R = 89 %). Eb. : $152^{\circ}/760 \text{ mm}$

I.R. (film) : 3350 - 2100 - 2180 N.M.R. 13C : 32.1 ; 31.4 ; 25.2 ; 22.4 ; 13.8 .

V - octynes $d_2^{-3}, 3$ (<u>8a</u>); $d_2^{-4}, 4$ (<u>8b</u>); $d_2^{-5}, 5$ (<u>8c</u>); $d_2^{-6}, 6$ (<u>8d</u>)

General procedure : the reaction is performed under a dry nitrogen atmosphere . To a 2M solution of lithium acetylide-ethylene-diamine complex (4 mmoles) in dry DMSO, brought to 8° are added dropwise the labelled bromo-alkane (3.8 mmoles) 6. The solution is stirred for one hour and allowed to warm up to room temperature (one hour)

The flask is then cooled and water is carefully added . Octynes are distilled directly from the hydrolysed reaction using a Dean-Stark trap . The separated organic layer is dried over calcium chloride (R = 83 %). I.R. (film): 3300 - 2190 - 2100N.M.R. 13C octyne: 84.6; 67.9; 31.2; 28.3; 22.4; 18.3; 13.9N.M.R. 13C labelled octynes: $\Delta\delta_2^2$ D shift = 0.2 ppm upfield.

VI - alkynes dicobalt hexacarbonyl complexes (8a to 8d)

3 mmoles of alkyne and 1.2 g of dicobalt octacarbonyl (3 mmoles + 10 %) are both dissol-

ved in 15 ml of pentane . Carbon monoxide is allowed to evolved for three hours . The reaction mixture is filtered on silica gel . Pentane is removed and hexacarbonyl dicobalt complex is obtained as a deep red oil .

I.R. (CC1₄) : 2020 - 2040 - 2080 N.M.R. 13C octyne complex : 97.5 ; 73.0 ; 34.1 ; 31.8 ; 31.4 ; 28.9 ; 22.5 ; 13.9

N.M.R. 13C labelled octype complexes : $\Delta\delta_2^2$ D shift = 0.2 ppm upfield.

REFERENCES

- R. ROWAN and B. SYKES, J. Am. Chem. Soc., <u>96</u>, 7000 (1974)
 C. CHACHATY, Z. WOLKOWSKY, F. PIRIOU and G. LUKACS, J. Chimie Physique, <u>71</u>, 487 (1974)
 A. A. RIBEIRO and E. A. DENNIS, J. Phys. Chem., <u>81</u>, 957 (1977)
 J. M. BERNASSAU and M. FETIZON, Tetrahedron, <u>37</u>, <u>7105</u> (1981)
 R. V. HOSUR and G. GOVIL, Org. Magn. Res., <u>17</u>, 71 (1981)
 A. TCHAPLA and C. FABRE, Tetrahedron, <u>38</u>, <u>2147</u> (1982)
 Y. K. LEVINE, P. PARTINGTON and G. C. R. ROBERTS, Mol. Phys., <u>25</u>, 497 (1973) 2
- 4
- 5
- 6

- Y. K. LEVINE, N. J. M. BIRDSALL, A. G. LEE, J. C. METCALFE, P. PARTINGTON and G.C.K. ROBERTS, 8 J. Chem. Phys., 60, 2890 (1974)
 9 R. E. LONDON and J. AVITABILE, J. Am. Chem. Soc., 99, 7765 (1977)
 10 G. LIPARI and A. SZABO, J. Am. Chem. Soc., 104, 4546 (1982)
 11 N. BELLAVITA, J. M. BERNASSAU, P. CECCHERELLI, M. S. RAJU and E. WENKERT, J. Am. Chem. Soc., 104, 100 and 10

- <u>102</u>, 17 (1980)
- A. I. VOGEL, Practical Organic Chemistry (3^d ed.), p. 277-294, Longmans, London (1956) ibid., p. 240 12
- 13 14
- 15
- H. GILMAN and A. H. BLATT, Org. Synth. Coll., Vol. I, p. 306 H. GILMAN and A. H. BLATT, Org. Synth. Coll., Vol. I, p. 361 W. NOVIS SMITH and O. F. BEUMEL, JR., Synthesis, 441 (June 1974) 16
- 17 H. GREENFIELD, H. W. STERNBERG, R. A. FRIEDEL, J. H. WOTIZ, R. MARKBY and I. WENDER, J. Am.

- H. GREENFIELD, H. W. STERNBERG, R. A. FRIEDEL, J. H. WUI12, R. MARKOI aiki I. MINDLE, C. CHER. Soc., 78, 120 (1956)
 D. E. DORMAN, M. JAUTELAT and J. D. ROBERTS, J. Org. Chem., 38, 1026 (1973)
 J. M. KORNPROBST and J. P. DOUCET, J. Chimie Physique, 71, 1129 (1974)
 J. E. DUBOIS and J. P. DOUCET, Org. Magn. Res., 11, 87 (1978)
 F. D. GUNSTONE, M. R. POLLARD, C. M. SCRIMGEOUR, N. W. GILMAN, B. C. HOLLAND, Chem. and Phys. of Lipids, 17, 1 (1976)
 W. HOBOLD, R. RADEGLIA and D. KLOSE, J. Prakt. Chem., 318, 519 (1976)
 A. BARABAS, A. A. BOTAR, A. GOCAN, N. POPOVICI and F. HODOSAN, Tetrahedron, <u>34</u>, 2191 (1978)
 C. CANFT. G. C. LEVY and I. R. PEAT. J. Magn. Res., 18, 199 (1975).

- 24 D. CANET, G. C. LEVY and I. R. PEAT, J. Magn. Res., 18, 199 (1975) .