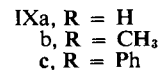
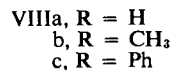
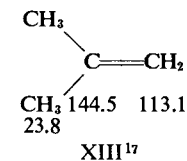
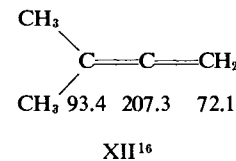
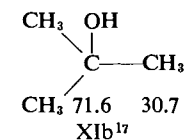
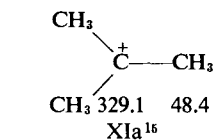
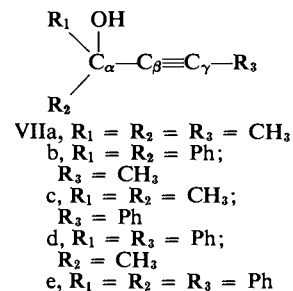
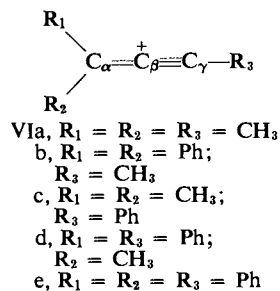
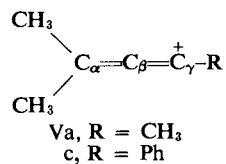
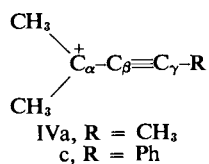


Table I. Cmr Data of the Alkynylcarbenium Ions VIa-e^{a,c} and Their Precursor Alcohols VIIa-e^{a,c}

Compd	C _α	C _β	C _γ	C _α CH ₃	C _γ CH ₃	C _α phenyl				C _γ phenyl					
						C _{ipso}	C _o	C _m	C _p	C _{ipso}	C _o	C _m	C _p		
VIa ^a	269.0	110.6	219.1, <i>J</i> _{CH₃,C_γ} = 9.8 (141.4)	43.7	14.0										
Vib ⁱ	(204.0) 195.7	(26.0) 93.2, <i>J</i> _{CH₃,C_β} = 4.4 (10.9)	165.1, <i>J</i> _{CH₃,C_γ} = 11.6 (81.7)	(12.7)	(11.2) 9.1	144.8	141.5	131.4	145.4						
VIc ^j	(121.6) 237.1	(28.1) 123.5	(116.5) 199.4	(7.7) 38.5	(5.8)	(-0.7)	<i>d</i>	<i>d</i>	(18.1)	119.9	141.7	131.4	145.5		
VI d ^j	(170.4) 200.8	(28.1) 111.1	(116.5) 167.5	(7.7) 28.8	(5.8)	140.8	141.0, ^e 140.2	131.7	148.9	119.9	139.0	130.8	137.0		
VI e ^j	(130.7) 186.8	(18.6) 105.9	(83.3) 159.1	(-4.2) 159.1	(-4.2)	(-4.7)	<i>d</i>	<i>d</i>	(21.4)	(-2.5)	<i>d</i>	<i>d</i>	(8.8)		
VII a ^k	(112.3) 65.0	(14.4) 84.6	(72.5) 77.7	(7.7) 31.0	(5.8)	(-5.9)	<i>d</i>	<i>d</i>	(21.5)	(-2.0)	<i>d</i>	<i>d</i>	(9.6)		
VII b ^l	74.1	82.3, <i>J</i> _{CH₃,C_β} = 4.0	83.4, <i>J</i> _{CH₃,C_γ} = 10.5		3.3	145.5	127.9 ^o	125.7	127.3						
VII c ^m	66.7	95.4	82.9	30.8						123.0	129.4 ^o	132.3	129.4		
VII d ^l	70.1	92.5	84.2	33.0		145.5	125.0 ^o	128.2	127.5	122.4	128.2 ^o	131.6	128.2		
VII e ^l	74.5	91.5	86.6			144.6	125.7 ^o	128.0	127.4	121.9	128.0 ^o	131.4	128.0		

^a The coupling constants (in Hz) were obtained directly from the spectra recorded without proton decoupling. ^b The numbers in parentheses refer to the difference in chemical shift between the ion and precursor. ^c Chemical shifts are in ppm from TMS. ^d Assignment of C_o and C_m in precursor is uncertain. ^e Two peaks each of intensity one carbon. ^f It is assumed that the intensity of the carbons in the C_α-phenyl will be approximately twice those of the C_γ-phenyl. ^g Alternative assignments. ^h In FSO₃H-SbF₅-SO₂ClF at -80°. ⁱ In FSO₃H-SbF₅-SO₂ClF at -60°. ^j In FSO₃H-SbF₅-SO₂ at -60°. ^k In SO₂ClF at -60°. ^l In CDCl₃ at 35°. ^m In SO₂ at -40°.

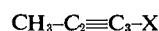


contributions of the mesomeric forms IV and V to be made, and indicate significant contributions from the allenyl form V in the former (VIa-e) but not the latter (VIIIa-c) examples.

The preparation of the alkynylcarbenium ions VIa-e from their alcohol precursors, VIIa-e, respectively, has been reported previously⁸ (the present work utilized these preparations with some improvement on the methods used previously and is described in the Experimental Section). The novel alkynoyl cations VIIIa-c were generated from their corresponding acyl fluorides IXa-c¹² using antimony pentafluoride in sulfur dioxide solution (the preparation of VIIIa-c and IXa-c is fully described in the Experimental Section and the relevant ¹H and ¹⁹F parameters are summarized in Table III).

The carbon-13 nmr spectra were obtained by the fast Fourier transform method¹³ on a Varian Associates XL-100 spectrometer.

The cmr data for the ions VIa-e and their precursor alcohols VIIa-e are given in Table I. The assignment of C_α, C_β, and C_γ did represent some difficulty but it was possible to identify C_γ in VIa and VIb by the large long-range coupling to the C_γ-CH₃ protons in the spectra obtained without proton decoupling. Dreeskamp, *et al.*¹⁴ have determined the geminal and vicinal ¹³C-¹H coupling constants in a number of methylacetylenes (Xa-c) shown below. The analogous coupling constants were



- Xa (X = H),^{14a} $J_{\text{CH}_2, \text{C}_2} = 10.6$ Hz; $J_{\text{CH}_3, \text{C}_3} = 4.8$ Hz
 b (X = CH₂Cl),^{14b} $J_{\text{CH}_2, \text{C}_2} = 8.2$; $J_{\text{CH}_3, \text{C}_3} = 4.3$
 c (X = CH₂Br),^{14b} $J_{\text{CH}_2, \text{C}_2} = 7.9$; $J_{\text{CH}_3, \text{C}_3} = 4.7$

determined in VIa, VIb, VIIa, and VIIb (Table I) and they clearly differentiate C_γ, C_β, and C_α. There was no observable coupling between the C_γ-CH₃ and C_α in these four examples while the inability to observe a coupling between the C_γ-CH₃ and C_β in VIa and VIIa is probably due to the broadening of the C_β signal by smaller long-range coupling to the C_α-CH₃ protons. The aromatic and methyl resonances were identified by "off-resonance" decoupling experiments.

The marked deshielding of C_α and C_γ in the ions VIa-e relative to their precursor alcohols VIIa-e (Table I, shown in brackets) clearly indicate substantial contribution from the mesomeric vinylic cation form V in all cases; positive charge at C_α should result in some deshielding of C_β (compare XIa and b, below) while C_γ should not be significantly affected. Aromatic substitution at C_α and C_γ results in these carbons becoming less deshielded in the carbocations relative to their precursor alcohols and this is consistent with the expected lessening of positive charge at C_α and C_γ by delocalization into the phenyl rings. There is clearly more delocalization of charge into the C_α-phenyl group since the para carbon in the C_α-phenyl group in VIc and e (Table I) is significantly more deshielded, relative to the precursor alcohols VIId and e, than is the para carbon of the C_γ-phenyl group.

To estimate the relative contributions of the mesomeric forms IVa and Va in VIa, we have chosen, as a

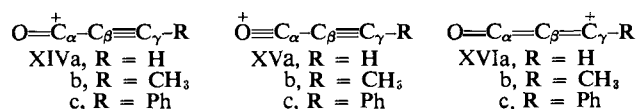
model for the C_α carbon in the mesomeric form IVa, the *tert*-butyl cation XIa,¹⁵ where the central carbon is deshielded by 257.5 ppm relative to its precursor 2-methyl-2-propanol (XIb). 3-Methyl-1,2-butadiene (XII)¹⁶ was considered as a model for C_α in Va, but the deshielded central carbon of the allene is not reflected in the chemical shift of C_β in the ions VIa-e; this is presumably due to the sp hybridization of C_γ in Va. Therefore, 2-methyl-2-propene (XIII) was used as a model—it is expected that the positive charge at C_γ will not have a significant effect on the chemical shift of C_α in Va; thus C_α should be deshielded by 79.5 ppm (= 144.5 - 65.0) relative to the precursor VIIa (Table I).

Experimentally C_α is deshielded by 204.0 ppm in VIa relative to VIIa and substituting the values from the model compounds (above) reveals that the relative contributions of IVa and Va are in the ratio of about 2:1. This conclusion is supported by the fact that the deshielding of C para in the C_α-phenyl group of VIc is approximately twice that of C para in the C_α-phenyl group, consistent with the amount of positive charge at C_α being approximately twice that at C_γ.

For the ion VIc, XIa and b serve as suitable models for mesomeric form IVc ($\Delta C_\alpha = 257.5$ ppm) while XIII serves as a model for Vc ($\Delta C_\alpha = 144.5 - 66.7 = 77.8$ ppm). C_α is deshielded by 170.4 ppm in VIc relative to VIIc and this represents equal contributions of IVc and Vc in VIc. Schiavelli concluded, on the basis of his solvolytic studies of haloallenes,^{10a-d} that the intermediate allenyl cations (including VIe from 1-chloro-1,3,3-triphenylallene) were extensively delocalized with more charge residing at C_α than C_γ, consistent with our conclusions. It should be noted, however, that the charge distributions are not reflected in the subsequent reactions of these ions since attack by solvent occurs exclusively at C_α to give propargyl alcohols unless C_α is sterically hindered (*i.e.*, VI, R₁ = R₂ = *t*-Bu, R₃ = *t*-Bu or Ph), where 10-15% of the solvolyzed products originated from attack at C_γ.^{10a,c}

The results for VIa indicate that where there is competitive charge localization in a carbocation, a tertiary carbenium center (*i.e.*, the positive charge residing at C_α) localizes approximately twice the charge as does a secondary vinylic cation center¹⁸ (*i.e.*, the charge residing at C_γ). When C_γ is a secondary benzylic vinyl cation¹⁸ (Vc, VIc), the charge localization at C_γ is approximately equal to that of a tertiary carbenium center.

The alkynoyl cations VIIIa-c, prepared from their parent alkynoyl fluorides IXa-c (see Experimental Section), can exist in the mesomeric forms XIVa-c, XVa-c, and XVIa-c, of which the latter are vinyl cations. The cmr, pmr, and fmr data for VIIIa-c and IXa-c are given in Tables II and III, respectively.



The C_α, C_β, and C_γ resonances were readily differen-

(12) VIIIc can also be generated from the more readily accessible phenylpropynoyl chloride, using the same conditions.

(13) (a) R. Ernst, *Advan. Magn. Resonance*, **2**, 108 (1966); (b) R. Ernst and W. A. Anderson, *Rev. Sci. Instrum.*, **37**, 93 (1966).

(14) (a) H. Dreeskamp, E. Sackman, and G. Stegmeier, *Ber. Bunsenges. Phys. Chem.*, **67**, 860 (1963); (b) H. Dreeskamp and E. Sackman, *Z. Phys. Chem.*, **34**, 273 (1962).

(15) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969).

(16) R. Steur, J. Van Dongen, M. DeBie, and W. Drenth, *Tetrahedron Lett.*, 3307 (1971).

(17) In SO₂ solution at -40°.

(18) The term "primary" has been used previously^{3d} for the C=C⁺-H ion.

Table II. Cmr Data of the Alkynoyl Cations VIIIa-c^{a-c} and Their Precursor Acyl Fluorides IXa-c^{a,c}

Compd	C _α	C _β	C _γ	CH ₃	C _{ipso}	C _o	C _m	C _p
VIIIa ^d	124.1, J _{C_α,H} = 7.6 (-17.6)	48.9, J _{C_β,H} = 54.4 (-20.2)	110.7, J _{C_γ,H} = 294.9 (28.3)					
VIIIb ^d	124.2, J _{C_α,H} = 2.2 (-18.3)	45.9, J _{C_β,H} = 3.5 (-21.5)	130.8, J _{C_γ,H} = 11.0 (36.4)	8.6, J _{CH} = 138.8 (5.6)				
VIIIc ^d	124.2 ^f (-25.5)	56.9 (-26.9)	134.2 ^f (39.3)		107.1 (-9.8)	141.8 (7.6)	131.2 (1.8)	143.0 (9.9)
IXa ^e	141.7, J _{C_α,H} = 5.7, J _{C_α,F} = 318.4	69.1, J _{C_β,H} = 51.7, J _{C_β,F} = 105.8	82.4, J _{C_γ,H} = 265.3, J _{C_γ,F} = 14.5					
IXb ^e	142.5, J _{C_α,H} < 1.5, J _{C_α,F} = 315.7	67.4, J _{C_β,H} = 3.5, J _{C_β,F} = 103.5	94.4, J _{C_γ,H} = 10.5, J _{C_γ,F} = 14.1	3.0, J _{CH} = 133.3, J _{CF} < 1.5				
IXc ^e	149.7, J _{C_αF} = 313.9	83.8, J _{C_β,F} = 103.1	94.9, J _{C_γ,F} = 14.0		117.3	134.2	129.4	133.1

^a The coupling constants (in Hz) were obtained directly from the spectra recorded without proton decoupling. ^b The numbers in parentheses refer to the difference in chemical shift between the ion and precursor. ^c Chemical shifts are in ppm from TMS. ^d In SbF₅-SO₂ at -40°. ^e In SO₂ at -40°. ^f The alternate assignment is equally possible.

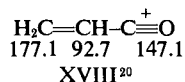
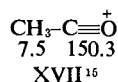
Table III. Pmr and Fmr Data for the Alkynoyl Cations VIIIa-c^{a,b} and Their Precursor Acyl Fluorides IXa-c^{a,c}

Compd	HC≡C	CH ₃	H _o	H _m	H _p	F
VIIIa ^d	5.21 (1.85)					
VIIIb ^d		2.94 (1.15)				
VIIIc ^d			8.22 (~1.02)	7.60 (~0.40)	8.02 (~0.82)	
IXa ^e	3.36, J _{H,F} < 0.5					-47.94
IXb ^e		1.79, J _{H,F} = 2.3				-47.91
IXc ^e			~7.2	~7.2	~7.2	J _{H,F} = 2.3 -47.41

^a Proton chemical shifts are in ppm from TMS (capillary) and coupling constants are in Hz. ^b The numbers in parentheses refer to the difference in chemical shift between the ion and precursor. ^c Fluorine chemical shifts are in ppm from CFCl₃ (capillary) and coupling constants are in Hz. ^d In SbF₅-SO₂ at -40°. ^e In SO₂ at -40°.

tiated in IXa-c by the ¹³C-¹⁹F coupling constants. These coupling constants rapidly diminish as the ¹³C-¹⁹F distance increases until, in IXb and c, there is no measurable coupling between the methyl carbon, or the ipso carbon, and the acyl fluorine. A similar distance effect has been observed in fluoronorbornanes.^{19a} Interestingly, there is a substantial value of ⁵J_{H,F} in IXb but a negligible ⁴J_{H,F} in IXa; this is presumably due to the fact that there is no π contribution to the coupling mechanism in the latter case.^{19b} The long-range ¹³C-¹H couplings were also determined in IXa and b, and in VIIIa and b, thereby distinguishing the C_α, C_β, and C_γ resonances in the ionic species. However, it was not possible to positively identify C_α, C_β, C_γ, or C_{ipso} in VIIIc but C_β and C_{ipso} were assigned by analogy with the results for VIIIa and b (Table II) and VIc, d, and e (Table I); the assignment of C_α and C_γ in Table II is speculative and could be reversed.

The cmr data for the alkynoyl cations VIIIa and b (Table II) are interesting in that C_α and C_β are substantially shielded relative to the precursors IXa and b while C_γ is deshielded. The cmr parameters for the acetylium ion (XVII)¹⁵ and the propenoyl cation (XVIII)²⁰ are shown below for comparison. The data indi-



(19) (a) J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 7107 (1970); (b) M. Barfield and S. Sternhell, *ibid.*, **94**, 1905 (1972).

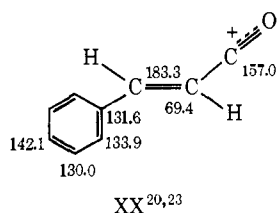
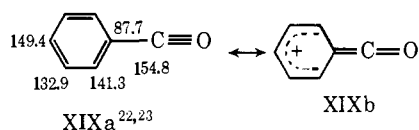
(20) G. A. Olah, J. M. Denis, and P. W. Westerman, *J. Org. Chem.*, in press.

cate that the oxonium forms XVa and b are the predominant mesomeric contributors and the mutual shielding of the two sp carbons (C_α and C_β) gives rise to the substantial upfield shifts observed for these two carbons. Similar shielding is observed for the C_{ipso} resonances in ethynylbenzenes and benzonitriles.^{21a,b} Although C_γ is deshielded in VIIIa and b relative to IXa and b (Table II), the difference is much smaller than is observed for C_γ in the ions VIa-c (Table I) and it must be concluded that the mesomeric forms XVIa and b and XIVa and b make only a small contribution to the total structure of these ions. Indeed, whereas the alkynylcarbenium ions VIa-e are all deep red in color, the alkynoyl ions VIIIa and b are pale yellow, suggesting that there is less extensive charge delocalization. The fact that it was not possible to prepare the ions H-C≡C⁺CR₂, R = alkyl or aryl, while VIIIa is quite stable, is also indicative of the high contribution from the oxonium form XVa, but this does not necessarily (although it is likely) result from the delocalization factor alone.

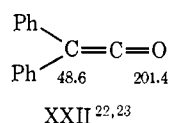
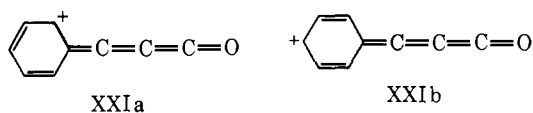
In contrast, the phenyl-substituted ion VIIIc is of deep red-orange color and the pmr (Table III) and cmr (Table II) spectra indicate that there is substantial delocalization of charge into the ortho and para aromatic positions since these carbons, and their attached protons, are deshielded relative to the meta carbons and protons. However, the only change in C_α, C_β, or C_γ in VIIIc relative to VIIIb is that C_β is somewhat deshielded—the position of C_α and C_γ is virtually un-

(21) (a) G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Amer. Chem. Soc.*, **94**, 3089 (1972); (b) J. Mason, *J. Chem. Soc. A*, 1038 (1971).

changed. The cmr data reported previously in our work for the benzoyl (XIXa)²² and 3-phenylpropenoyl (XX)²⁰ cations are shown for further comparison.

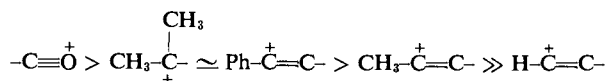


In the case of benzoyl cations,²² it was concluded that "ketene-like" mesomeric forms XIXb made a large contribution to the total ion structure. Comparison of the cmr data for VIIIc (Table II) and XIX leads to the conclusion that there is significant delocalization of positive charge onto C_o and C_p but not onto C_γ or C_α, and thus the mesomeric forms XVC and XXIa and b are the only significant resonance contrib-



utors. Because of the rather unique nature of the mesomeric forms XXIa and b, it is not possible to choose a model system for direct comparison. Indeed, the unusual cmr shift for allenic (*e.g.*, XII)¹⁶ and ketenic (*e.g.*, XXII)²² carbons indicate the limitations for comparison with model compounds.

From the above data, we conclude that the positive charge on the alkynoyl cations VIIIa and b resides almost exclusively on the oxygen atom while the ion VIIIc has significant delocalization of charge onto the ortho and para ring carbon atoms; C_γ does not appear to carry any substantial charge and the mesomeric vinylic forms XVIa-c make no significant contribution to the total ion structures. Since we have shown that the mesomeric vinyl (allenyl) cations contribute extensively to the total ion structures of the alkynylcarbenium ions VIa-e, we can combine these results to predict the positions at which charge will preferentially localize in a range of carbocations which can exist in two, or more, mesomeric forms. The trend shown below relates, from right to left, the increasing charge localization at these positions at the expense of other mesomeric forms



(22) G. A. Olah and P. W. Westerman, *J. Amer. Chem. Soc.*, **95**, 3706 (1973).

(23) Converted to δ ¹³C from external TMS from the original data given from external CS₂ using $\delta_{\text{TMS}}^{\text{CS}_2}$ 193.7.

Although ion stability is a combination of several factors, this may indeed represent the relative order of ion stability for carbocations containing these isolated fragments and thus it should, under suitable conditions, be possible to generate vinyl cations under stable, long-lived ion conditions. It cannot be overemphasized that vinyl cations are highly reactive species which are generated by a relatively slow ionization step, and it is highly likely that the inability, so far, to observe these ions under stable conditions is due to the reaction of the vinyl cations with un-ionized precursor and not due to any inherent instability.

Experimental Section

The precursors of the alkynylcarbenium ions VIa-e used in this study were commercially available or were prepared by standard methods.⁸

Propynoyl Fluoride (IXa). A mixture of propynoic acid (7 g) and benzoyl fluoride (37 g) was heated to 150°. The distillate boiling in the range 24-40° was collected and redistilled to give IXa (4.6 g) as a colorless liquid, bp 23-24° (lit.²⁴ bp 22-23°).

2-Butynoyl Fluoride (IXb). A mixture of 2-butynoic acid (5 g) and benzoyl fluoride (35 g) was heated to 150°. The distillate boiling in the range 67-80° was collected and redistilled to give IXb (3.6 g) as a colorless liquid, bp 77-78°: ν_{max} (neat liquid) 2440, 1810, 1225, 1008, and 746 cm⁻¹; mass spectrum (70 eV, 50°) *m/e* 86 (P⁺), 67 (P - 19⁺), 58, 57, 43, 39. Cmr data are given in Table II, and pmr and fmr data are given in Table III.

Phenylpropynoyl Fluoride (IXc). Selenium tetrafluoride²⁵ (4.5 g) was added dropwise, with stirring, to a slurry of sodium phenylpropynoate (from phenylpropynoic acid (3.65 g)) in benzene (30 ml) at 0°. The mixture was stirred overnight at room temperature and worked up by the addition of water. IXc was obtained as a colorless liquid (0.8 g), bp 76-78° (10 mm) (lit.²⁶ bp 53° (2 mm)).

Preparation of Ions. The preparation of the alkynylcarbenium ions VIa-e has been described previously.⁸ It was found, in this study, that if the carbocations VIa and b were generated by the addition of solutions of VIIa and b, respectively, in SO₂ClF at -130° to a rapidly stirred (shaken) solution of 1:1 SbF₅-FSO₃H in SO₂ClF at -130°, by-product formation was completely avoided. The pmr spectrum of VIa in SO₂ClF at -80° was slightly different to that reported previously in SO₂ solution at -60°:⁸ C_α-CH₃, δ 3.70 (q, *J*_{CH₃,CH₃} = 2 Hz); C_γ-CH₃, δ 3.50 (septet).

The alkynoyl cations VIIIa-c were prepared by adding a solution of the corresponding fluorides, IXa-c, respectively, in SO₂ at -80° to a slurry of SbF₅ in SO₂ at -80°. The resulting mixtures were allowed to warm up to -40° to afford complete dissolution and ionization.

Proton and Fluorine Magnetic Resonance Spectroscopy. Pmr and fmr spectra were obtained using a Varian Associates Model A56/60A nmr spectrometer equipped with a variable-temperature probe. External TMS (capillary) and CFC₃ (capillary) were used as a reference for pmr and fmr spectra, respectively.

Carbon-13 Nuclear Magnetic Resonance Spectroscopy. Cmr spectra were obtained using a Varian Associates Model XL-100 nmr spectrometer equipped with a broad-band decoupler, Fourier transform accessory, and a variable-temperature probe. The spectrometer was operated at 25.16 MHz and was interfaced with a Varian 620-L computer. Chemical shifts were measured from the ¹³C signal of 5% ¹³C-enriched TMS in a 1.75-mm capillary held concentrically inside the standard 12-mm sample tube. Coupling constants were obtained directly from the cmr spectra measured without proton decoupling.

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