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Cyclopropylcyclopropylidenemethyl Cation: A Unique Stabilized Vinyl Cation Characterized by NMR Spectroscopy and Quantum Chemical ab Initio Calculations

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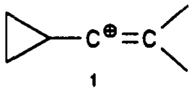
Abstract: The cyclopropylcyclopropylidenemethyl cation is generated by protonation of bis(cyclopropylidene)methane. The NMR spectroscopic data, below −135 °C, demonstrate the charge delocalization due to C,C-hyperconjugation. Quantum chemical ab initio calculations at the correlated level (MP2/6-31G*) support the interpretation of the experimental results and reveal the geometrical consequences of σ-C,C-hyperconjugation. ^{13}C NMR chemical shifts have been calculated by using the GIAO-SCF and GIAO-MP2 method. The experimental shifts are satisfactorily reproduced only at the correlated GIAO-MP2 level, thus showing the importance of electron correlation for a correct theoretical description of vinyl cations. The cyclopropylcyclopropylidenemethyl cation is the first vinyl cation prepared in solution which is stabilized only by hyperconjugative interaction with C,C-σ-bonds.

The stabilizing effect of cyclopropyl substituents in carbocations is well documented.[1] In vinyl cations a cyclopropyl ring can be attached to the C^+ carbon either, as in **1**, by a single bond, like in trigonal carbocations, or, as in **2**, by a double bond. In the cyclopropylidenemethyl cation type structure (**2**) the cyclopropane ring is part of the vinyl cation double bond. Combination of both substructures **1** and **2** leads to the cyclopropylcyclopropylidenemethyl cation structure (**3**), an unsaturated analogue of the dicyclopropylmethyl cation (**4**). As both cyclopropyl rings can contribute in the delocalization of the positive charge, **3** may be expected to be a particularly stabilized vinyl cation. Cation **3** has been postulated to be a reactive intermediate in solvolysis and rearrangement reactions.[2–4] However, the preparation of **3** as a long-lived cation in solution by SbF_5-assisted heterolysis of the sp^2 C–X bond of cyclopropylcyclopropylidenemethyl halides[5] has failed as well as earlier attempts to generate **3** by protonation of bis(cyclopropylidene)methane (**5**) using superacids.[6]

We have now successfully prepared and characterized the vinyl cation **3** at very low temperature in solution. In addition we have performed a computational investigation of **3**. The structure of **3** has been optimized at the MP2/6-31G* level of theory, and quantum chemical calculations for the ^{13}C NMR chemical shifts have been carried out in order to confirm the assignment of the experimental NMR spectrum.



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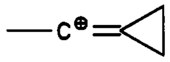

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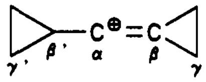

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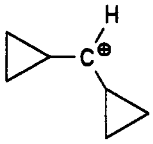

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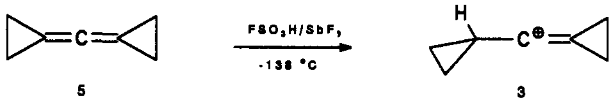

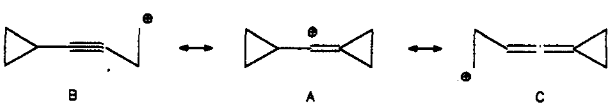

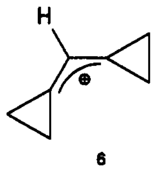

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Results and Discussion

The protonation of bis(cyclopropylidene)methane (**5**)[8a,b] with FSO_3H/SbF_5 was carried out by cocondensation onto a surface

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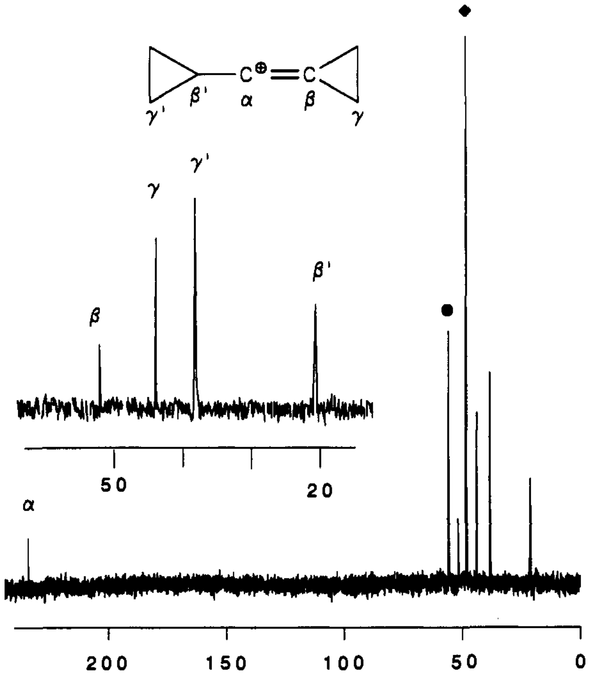


Figure 1. ^{13}C NMR (100.6 MHz) spectrum of cation **3** at −138 °C in SO_2ClF/SO_2F_2: (●) reference $\delta(NMe_4^+)$ = 55.65 ppm; (◆) CH_3 group of *tert*-butyl cation = 48.24 ppm, *tert*-butyl C^+ signal δ = 335.43 ppm omitted; inset (15–60 ppm) signals of **3** only.

Table 1. ^{13}C NMR and ^{1}H NMR Spectral Data for Vinyl Cation **3**[a]

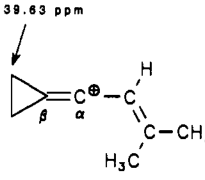
	α	β	β'	γ	γ'
^{13}C[b,d]	234.18	51.67	21.21 d (193.5)	43.90 t (178.0)	38.15 t (176.0)
^{1}H[c,d]			2.89	2.95–2.81	3.8–3.6

[a] Chemical shifts δ in ppm, coupling constants $^1J_{CH}$ in Hz (in parentheses). [b] 100.62 MHz, at −138 °C in SO_2ClF/SO_2F_2, internal reference $\delta(NMe_4^+)$ = 55.65 ppm (chemical shifts ±0.03 ppm, coupling constants ±2.6 Hz). [c] 400 MHz, −138 °C in SO_2ClF/SO_2F_2, internal reference $\delta(NMe_4^+)$ = 3.00 ppm (chemical shifts ±0.002 ppm). [d] Additional signals (*tert*-butyl cation): ^{13}C 335.43, s, 48.24, q (131.7 Hz); ^{1}H 3.75.

cooled to liquid nitrogen temperature. Details of the experimental technique have been described earlier.[7] The ^{13}C NMR (Figure 1) and ^{1}H NMR spectra of the orange reddish solution in SO_2ClF/SO_2F_2 were measured at −138 °C. Besides from signals which could be assigned to the *tert*-butyl cation, formed in increasing amount at higher temperatures, probably by a fragmentation process, the spectra indicate the exclusive formation of cation **3**. The isomeric allyl cation **6**, which would result from proton attack at the central allenic carbon of **5**, was not observed. The assignments of the ^{13}C NMR signals of **3** (Table 1) were made using ^{1}H-coupled and single-frequency ^{1}H-decoupled ^{13}C NMR spectra, by comparison with other vinyl cations,[9–14] and are supported by GIAO-MP2 calculations of the chemical shifts (see below).

NMR Spectroscopic Results

The chemical shift of the signal of the C^+ carbon in **3** (234.18 ppm) is about 20 ppm at higher field than in the trigonal analogue, the dicyclopropylmethyl cation (**4**) (253.7 ppm).[15] Comparable shifts for the C^+ carbon have been observed in vinyl cations stabilized by π-conjugating substituents or β-silyl groups.[9–14] The chemical shift of the doubly bound C_β carbon (51.67 ppm) in **3** is about 20–30 ppm upfield compared to that in other vinyl cations.[11–14] As in other cyclopropylidenemethyl cations like **7**[10] and **8**,[16] the large shielding is due to the unique structure of these cations where the olefinic C_β carbon is also part of the cyclopropyl ring.



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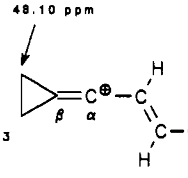

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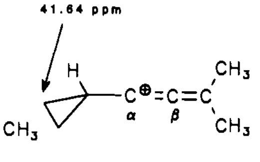

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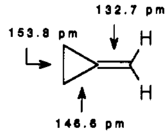

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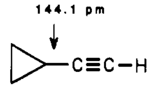

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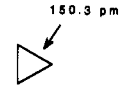

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The signal of the cyclopropyl methine carbon $C_{\beta'}$ (21.21 ppm) is about 20–40 ppm upfield shifted compared to the corresponding signal for cyclopropyl-substituted trigonal carbocations (dicyclopropylmethyl cation (**4**), 38.7 ppm[15]; (dimethylcyclopropyl)methyl cation 60 ppm.[17] The relatively high field shift of $C_{\beta'}$ in **3** compared to **4** is due to a shielding effect of the sp-hybridized C_α carbon in **3**. Compared to the shift of the cyclopropyl methine carbon in cyclopropylacetylenes (0–1 ppm),[18,19] the corresponding signal for $C_{\beta'}$ in **3** is deshielded however by ~20 ppm. The size of the $^1J_{CH}$ coupling constant of $C_{\beta'}$ (doublet, $^1J_{CH}$ 193.5 Hz) is in accord with those in other α-cyclopropyl-substituted vinyl cations.[18] The ^{13}C signals at 43.90 ppm ($^1J_{CH}$ 178.0 Hz) and 38.15 ppm ($^1J_{CH}$ 176.0 Hz) were specifically assigned to the γ- and γ'-methylene groups, respectively, by single-frequency ^{1}H-decoupling. On proton decoupling at 3.8–3.6 ppm the triplet at 43.90 ppm collapsed to a single peak, whereas the signals of the CH_2 groups at 38.15 ppm and the signals of the CH group at 21.21 ppm showed no effect. This assignment is in accord with those in other α-cyclopropyl vinyl cations[11,18,19] and in the cyclopropylidene-substituted vinyl cations **7** and **8**[10,16] and is also confirmed by GIAO-MP2 calculations of NMR chemical shifts (see below). The cyclopropyl CH_2 carbons C_γ in **3** are 3.5 ppm less deshielded than in the α-cyclopropyl allenyl cation **9** (41.64 ppm),[11] suggesting that, in α-cyclopropyl-substituted vinyl cations of type **1**, a β-cyclopropylidene group, as in **3**, is somewhat more efficient in stabilizing the positive charge than the β-isopropylidene group in cation **9**.

The chemical shift for the cyclopropylidene γ-CH_2 groups is 43.90 ppm in **3**, compared with 39.63 ppm[10] in the related cyclopropylidenemethyl cation **7** and 48.10 and 49.76 ppm in (*E*)-**8** and (*Z*)-**8**, respectively.[16] The hyperconjugational effect of an α-cyclopropyl substituent in cyclopropylidenemethyl type cations **2** is thus comparable to α-allyl type π-resonance stabilization. The charge-delocalizing ability of the α-cyclopropyl

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Table 2. Selected Calculated Bond Lengths (in pm) of 3 Obtained at the MP2/6-31G* Level

C_α–C_β	125.1	C_α–$C_{\beta'}$	137.3
C_β–C_γ	152.5	$C_{\beta'}$–$C_{\gamma'}$	157.3
C_γ–C_γ	146.8	$C_{\gamma'}$–$C_{\gamma'}$	145.0
$H_{\beta'}$–$C_{\beta'}$	108.5	H_γ–C_γ	108.6
$H_{\gamma'}$–$C_{\gamma'}$ (anti)	108.4	$H_{\gamma'}$–$C_{\gamma'}$ (syn)	108.5

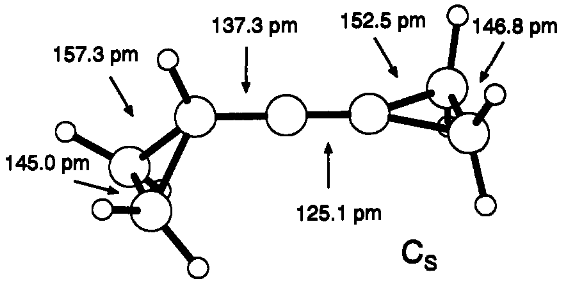

Figure 2. Calculated MP2/6-31G* geometry of cation 3 together with selected bond lengths.

ring in **3** is somewhat smaller than that of the α-isobutenyl substituent in **7** but greater than that of the α-propenyl substituent in **8**.

The delocalization of positive charge in the vinyl cation **3** can be explained qualitatively in terms of resonance of valence bond structures A ↔ B ↔ C. Hyperconjugative delocalization of the positive charge from the C^+ carbon into the cyclopropylidene group is described by contributions of no-bond homopropargyl-type resonance structures B, whereas hyperconjugative charge delocalization to the α-cyclopropyl ring is illustrated by contributions of no-bond homoallenyl-type resonance structures C. Hyperconjugation of the C,C-σ-bonds of the β-cyclopropylidene moiety is anticipated to be more important than those of the α-cyclopropyl ring because the orbital interaction for the former is via a shorter double bond and the β-σ-bonds are fixed in a coplanar arrangement with the formally vacant orbital at the C^+ carbon.

Computational Results

To further support the interpretation of the NMR spectroscopic results, we have performed quantum chemical ab initio calculations of the structure[20] and the ^{13}C NMR chemical shifts[21-23] for cation **3**. The fully optimized geometry of **3** as obtained at the MP2/6-31G* level of theory[20] (total energy −270.86194 hartree at MP2/6-31G*, with all electrons correlated) illustrates the structural consequences of delocalization of positive charge into the σ-framework of this cation (Table 2, Figure 2).

The bisected conformation provides maximum overlap of the vacant p-orbital at C_α with the orbitals of the C,C bonds of the α-cyclopropyl ring. The C_α–C_β bond in **3** (125.1 pm) is considerably shorter than the C,C double bond in cyclopropylidenemethane (**10**) (132.7 pm).[24] The C_β–C_γ bond in **3** (152.5 pm) is elongated by 5.9 pm compared to the analogous bond in cyclopropylidenemethane (**10**) (146.6 pm). These changes in bond lengths can be rationalized by contributions of the homopropargyl resonance structure B. Contribution of the homoallenyl resonance structure C in **3** is indicated by the 6.8 pm shortening of the C_α–$C_{\beta'}$ bond (137.3 pm) compared to the cyclopropyl-C–$C_{(sp)}$ bond in cyclopropylacetylene (**11**) (144.1 pm)[24] and by the 7.0 pm lengthening of the $C_{\beta'}$–$C_{\gamma'}$ bonds (157.3 pm) in comparison to the C,C bond in cyclopropane (**12**) (150.3 pm).[24] The distal methylene C,C bonds in both rings of **3** ($C\gamma$–$C\gamma$ = 146.8 pm; $C\gamma'$–$C\gamma'$ = 145.0 pm) are considerably shortened relative to the corresponding C,C bonds in cyclopropylidenemethane (**10**) (153.8 pm) and in cyclopropane (**12**) (150.3 pm), respectively. The antisymmetric HOMOs of both cyclopropyl rings in **3** have anti-bonding character between the CH_2 carbons. Charge transfer from the cyclopropyl ring to the formally empty p-orbital at the C^+ carbon reduces the electron density in the antisymmetric HOMO at the CH_2–CH_2 bonds, thus leading to a shortening of these bonds.

Table 3. Calculated Natural Charges for 3[25]

C-α	C-β	γ-CH_2	β′-CH	γ′-CH_2	β-(C_3H_4)	α-(C_3H_5)
0.410	−0.140	0.224	−0.123	0.203	0.308	0.283

The cyclopropylidene moiety shows greater structural changes compared to the standard structures than the singly bonded cyclopropyl ring, indicating a larger involvement of the double-bonded cyclopropyl ring in σ-delocalization of the positive charge. A larger contribution of homopropargyl resonance structures B than homoallenyl resonance structures C is also suggested by the calculated natural charges (NPA charge distribution)[25] (Table 3). More than half of the positive charge is delocalized to the CH_2 groups of the two cyclopropyl rings. The cyclopropylidene ring carries more charge (0.308) than the α-cyclopropyl group (0.283).

Quantum chemically calculated ^{13}C NMR chemical shifts[21] have been successfully used to establish in the past the validity of theoretically determined geometries for various structural types of carbocations.[26] However, for **3** the calculated ^{13}C chemical shifts obtained with the standard methods (IGLO[21] and GIAO-SCF[22]) deviate significantly from the experimental data (Table 4 and ref 27). It has been known for some time that SCF-based methods for calculating chemical shifts fail to describe the magnetic properties of unsaturated molecules such as allene[23b] or allyl cations.[28] To improve the agreement of theoretically and experimentally determined chemical shifts, the recently developed GIAO-MP2[23] method has been used, which allows for the first time the routine calculation of NMR chemical shift at an electron-

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Table 4. Calculated ^{13}C NMR Chemical Shifts (in ppm) for 3[a]

method//basis set	C_α	C_β	$C_{\beta'}$	C_γ	$C_{\gamma'}$
GIAO-SCF//dzp/dz	270.6	48.7	12.0	33.2	34.7
GIAO-SCF//tzp/dz	283.9	52.1	13.6	33.3	35.0
GIAO-MP2//dzp/dz	195.4	49.6	21.6	47.2	41.8
GIAO-MP2//tzp/dz	213.4	55.6	24.3	49.2	42.9

[a] dzp/dz: polarized ($\alpha = 0.8$) double-ζ basis for C and double-ζ basis for hydrogen. tzp/dz: polarized ($\alpha = 0.8$) triple-ζ basis for C and double-ζ basis for hydrogen. For a detailed description of the basis sets, see ref 32. The calculated absolute shieldings for TMS are 198.9(GIAO-SCF//dzp/dz), 193.1 (GIAO-SCF//tzp/dz), 205.7 (GIAO-MP2//dzp/dz), and 198.9 (GIAO-MP2//tzp/dz), respectively.

correlated level. The results obtained with different basis sets[32] are summarized in Table 4.

The GIAO-SCF data (as well as the IGLO-SCF data[27]) are in only poor agreement with experiment. The C^+ carbon chemical shift is calculated to far downfield (GIAO-SCF (dzp/dz basis), $\Delta\delta = 36$ ppm; GIAO-SCF (tzp/dz basis), $\Delta\delta = 50$ ppm), whereas the cyclopropyl carbon atoms are computed by GIAO-SCF to be too shielded (except C_β with tzp/dz basis). Especially the shift for the α-cyclopropyl methine carbon $C_{\beta'}$ deviates considerably from the experimental value. The GIAO-SCF calculation fails to reproduce even qualitatively the relative order of the chemical shift for the two different methylene carbon signals. Contrary to the experimental order, the cyclopropylidene CH_2 carbons C_γ are calculated to be more shielded than the cyclopropyl CH_2 carbons $C_{\gamma'}$. The chemical shifts calculated for 3 using the GIAO-MP2[23] method show for all but the C^+ carbon a generally better agreement with the experimentally observed values. This emphasizes the importance of electron correlation effects for the appropriate description of the magnetic properties of unsaturated carbocations, like the vinyl cation **3**. Similar improvements in chemical shift calculation by using the GIAO-MP2 method have also been reported for other unsaturated carbocations, like arenium ions[29] and substituted allyl cations.[30] For the C^+ carbon of cation 3 the correlation correction is apparently too large to be adequately described by the GIAO-MP2 method. Even with the largest basis sets employed in our computational study, the chemical shift of the C^+ carbon of cation 3 is calculated to be about 21 ppm too shielded. MP2 theory is known to exaggerate the importance of electron correlation in difficult cases,[23b,31] and higher orders of perturbation theory or coupled cluster methods[33] are required to rectify that problem. While the chemical shift of the C^+ carbon of cation 3 is calculated to be too shielded, the γ- and γ'-methylene carbons are computed about 5 ppm too deshielded. The error is larger for the γ-CH_2 groups of the cyclopropylidene ring, which is involved more in hyperconjugative charge delocalization than the singly bonded cyclopropyl ring. It seems that MP2 theory overestimates the importance of hyperconjugation effects on structure and energies and that the difference of the calculated GIAO-MP2 and experimental shifts can be rationalized assuming an overestimation of σ-delocalization effects. The effect of higher order correlation corrections on the calculated chemical shifts is not yet known. Overall, the GIAO-MP2 method is clearly superior to SCF-based methods for calculating chemical shifts in reproducing the experimental ^{13}C NMR chemical shifts for 3, although the GIAO-MP2 results are not entirely satisfactory with respect to the remaining discrepancy of about 20 ppm for the C^+ carbon of 3.

Conclusion

For the first time an alkyl-substituted allene is protonated to yield a persistent vinyl cation in solution. The cyclopropylcyclopropylidenemethyl cation (**3**) is the first vinyl cation prepared under stable ion conditions which is stabilized only by hyperconjugative interaction with C,C-σ-bonds. The NMR spectroscopic data demonstrate the charge delocalization due to C,C-hyperconjugation of the cyclopropyl rings. The MP2/6-31G*-optimized structure supports the interpretation of the experimental results and reveals the geometrical consequences of σ-C,C-hyperconjugation. GIAO-MP2 calculations of ^{13}C NMR chemical shifts are shown to be superior to IGLO and GIAO-SCF methods to reproduce the experimental shifts of this unsaturated carbocation and strongly support the validity of the calculated structure. The cyclopropylcyclopropylidenemethyl cation (**3**) is thus the first vinyl cation which is completely characterized by NMR spectroscopy and ab initio calculation of structure, energy, and chemical shifts.

Experimental Section

Bis(cyclopropylidene)methane (**5**)[8] was prepared using a modified literature procedure.[8a] ^{13}C NMR (63 MHz, CD_2Cl_2, 27 °C): δ 176.59 (s, central allenic C), 80.93 (s, terminal allenic C), 7.40 (t, $^1J_{CH} = 166.1$ Hz, CH_2). ^1H NMR: δ 1.51 (s). FT-IR (NaCl, film): 2060 (s, ν_{as} C=C=C).

Preparation of the Carbocation. The general experimental technique and the special apparatus for the generation of carbocations have been described.[7] At a pressure of 10^{-5} mbar 1.33 mmol of **5** and 8.7 mmol of FSO_3H were distilled synchronously through separate nozzles onto a homogeneous matrix of 1.38 mmol of SbF_5, 0.4 mL of SO_2F_2, 1.4 mL of SO_2ClF, and 10 mg of tetramethylammonium tetrafluoroborate (TMA) cooled to −196 °C. After completion of the cocondensation another 0.4 mL of SO_2F_2 and 1.4 mL of SO_2ClF were distilled onto the matrix. An orange reddish solution of **3** admixed with *tert*-butyl cation was obtained by warming up to −135 °C. The solution was transferred under high vacuum at −135 °C into 10-mm NMR tubes, which were then sealed under vacuum and stored at −196 °C.

^1H NMR and ^{13}C NMR spectra of the carbocation solutions were measured on a Bruker AMX 400 NMR spectrometer equipped with a variable frequency fluorine lock channel and a 10-mm $^{13}C/^1H/^{19}F/^2H$ probe, using the fluorine resonance of SO_2ClF or SO_2F_2 as an internal lock. TMA was used as internal standard (^1H NMR, Me_4N^+, $\delta = 3.0$ ppm; ^{13}C NMR, $\delta = 55.65$ ppm). The probe temperature was calibrated with a ^{13}C chemical shift thermometer using neat 2-chlorobutane[34] in a capillary in an NMR tube filled with SO_2ClF admixed with other solvents.

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