Silyl Cations

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$[Me_3Si][R\text{-}CB_{11}F_{11}]$—Synthesis and Properties**

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Dedicated to Professor Neil Bartlett on the occasion of his 75th birthday

The synthesis and stabilization of electrophilic cations requires chemically robust, weakly coordinating anions or the corresponding Lewis super acids. The *closo*-carboranes $[RCB_{11}F_{11}]^-$ with R = H, alkyl, or F, belong to the group of weakly coordinating anions that are resistant to fluoride abstraction.[1] Various salts of the parent clusters were reported as early as 1967,[2,3] while their fluorinated derivatives were only accessible 30 years later.[4] The $[CH_3CB_{11}F_{11}]^-$ anion is so inert that it is able to stabilize the extremely electrophilic $[Al(CH_3)_2]^+$ cation.[5] Although this compound was the first example of a salt of a dimethylaluminium cation, no spectroscopic or structural data for it have been reported to date.

Trimethylsilyl compounds of the type Me_3SiX are convenient reagents for the exchange of X against fluoride or chloride due to rapid formation of volatile Me_3SiF or Me_3SiCl. Thus, the combination of a Me_3Si group bound to a weakly coordinating anion should allow access to novel electrophilic cations in the condensed phase. Herein, we describe the synthesis and properties of $[Me_3Si][RCB_{11}F_{11}]$ (R = H (**1**), C_2H_5 (**2**)). The title compounds were prepared in a multistep sequence, the last step of which involves the reaction of the triphenylmethyl salts with Me_3SiH[6] as shown in Equation (1).

$$[Ph_3C][RCB_{11}F_{11}] + Me_3SiH \rightarrow [Me_3Si][RCB_{11}F_{11}] + Ph_3CH \qquad (1)$$
$$R = H\ (\mathbf{1}),\ C_2H_5\ (\mathbf{2})$$

The colorless, air- and moisture-sensitive compounds (IR and Raman spectra are shown in Figures S1 and S2 in the Supporting Information) can be conveniently purified by sublimation in high vacuum at 100–110 °C. $[Me_3Si][C_2H_5CB_{11}F_{11}]$ (**2**) undergoes an endothermic phase transformation at 65 °C at which point the crystals become transparent before melting at 75 °C, as determined by differential scanning calorimetry (DSC). Above 220 °C, exothermic decomposition with evolution of gas occurs (Figure S3 in the Supporting Information). The gaseous products contain CH_4, SiF_4, and other as yet unidentified compounds. Similarly, $[Me_3Si][HCB_{11}F_{11}]$ (**1**) also undergoes a phase transformation at 95 °C (which is less endothermic than the melting process) and melts without decomposition at 125 °C; exothermic decomposition occurs at 215 °C (Figure S4 in the Supporting Information).

In order to determine whether **1** and **2** are molecular adducts or salts, the conductivity of $[Me_3Si][C_2H_5CB_{11}F_{11}]$ (**2**) was measured under argon in a specially designed cell (see Figure S5 in the Supporting Information). For the melt at 90 °C, a conductivity of 2.5 mS cm^{-1} was determined. A 1 M solution in CH_3CN at room temperature also had a conductivity of 2.5 mS cm^{-1}. With this value, $[Me_3Si][C_2H_5CB_{11}F_{11}]$ displays a conductivity typical for an ionic liquid, which falls in the range 1.5–8 mS cm^{-1}.[7] In addition, with a melting point considerably below 100 °C, $[Me_3Si][C_2H_5CB_{11}F_{11}]$ can be classified as an ionic liquid.[8] However, in contrast to most ionic liquids, $[Me_3Si][C_2H_5CB_{11}F_{11}]$ is extremely reactive. The $[Me_3Si]^+$ cation rapidly reacts with HCl gas at room temperature to give the free acid, as shown in Equation (2) (see IR and Raman spectra in Figure S6 and IR spectrum of the gaseous reaction products in Figure S7 in the Supporting Information).

$$[Me_3Si][C_2H_5CB_{11}F_{11}] + 4\,HCl \rightarrow 3\,CH_4 + SiCl_4 + H[C_2H_5CB_{11}F_{11}] \qquad (2)$$

The formation of CH_4 and $SiCl_4$ is noteworthy, since, contrary to Equation (2), the adduct $Me_3SiNCB(CN)_3$ reacts with HCl to give Me_3SiCl and $H[B(CN)_4]$[9] as the only products. The new acid $H[C_2H_5CB_{11}F_{11}]$ is soluble in $(CD_3)_2O$. The broadened signal at $\delta = 15.3$ ppm in the ^1H NMR spectrum suggests a high acid strength. In the IR spectrum, broad, strong absorption bands at 1705, 1620 and 920 cm^{-1} are observed in addition to shifted bands of the anion (see the comparison of the IR spectra of Cs^+, H^+ and $[H(H_2O)_x][C_2H_5CB_{11}F_{11}]$ in Figure S8 in the Supporting Information). This spectrum, as well as the high melting point of 185 °C (with decomposition) suggests the formation of hydrogen-bonded aggregates in the solid state.

For the last two decades, the structures and spectroscopic properties of silyl cations have been studied in detail.[10–13] The C-Si-C angle or the deviation of the SiC_3 unit from planarity

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as well as the shift of the ^{29}Si NMR spectroscopy signal have been used as qualitative measures of the cationic character of R_3Si cations. Almost planar silyl cations have, to date, only been observed in salts with weakly coordinating anions and sterically demanding substituents on silicon (e.g. mesityl).[13] To avoid coordination of solvent molecules to the silyl cations, solid-state ^{29}Si CPMAS NMR spectra have also been recorded.[6,10–13] Melts or ionic liquids containing silyl cations, which, owing to isotropic cation–anion interactions, should contain planar silyl cations, have not been studied to date. The low melting point of $[Me_3Si][C_2H_5CB_{11}F_{11}]$ allows for complete NMR spectroscopic characterization of the $[Me_3Si]^+$ cation in the liquid phase without solvent. Table 1 summarizes our results and shows calculated data as well as data from the literature for comparison.[14]

Table 1: Experimental and computed NMR spectroscopy parameters of some trimethylsilyl species.[a]

Parameter[b]	Me_4Si[c]	Me_3SiCl[c]	Me_3SiF[c]	$[Me_3Si]^+$	$[Me_3Si]^+\cdots FH$	**2**[d]
$\sigma(^{29}Si)\ \perp$	329	279	277	−231	71	
$\sigma(^{29}Si)\ \parallel$	329	307	320	237	246	
$\delta(^{29}Si)$	0.0	40.4	37.3	404	200	
$\delta(^{29}Si)$ exptl	0.0	30.3	32.0			138
$\delta(^{13}C)$	0.0	4.3	0.4	14.9	4.7	
$\delta(^{13}C)$ exptl	0.0	3.4	−0.3			−2.6[e]
$^1J(^{29}Si^{13}C)$	−43.5	−49.4	−52.8	−31.4	−45.4	
$^1J(^{29}Si^{13}C)$ (FC)	−44.0	−50.7	−54.1	−37.9	−49.2	
$\lvert ^1J(^{29}Si^{13}C)\rvert$ exptl	51.0	57.7	60.5			53

[a] Shielding σ or chemical shift δ in ppm, coupling constant J in Hz. [b] Values computed with DFT methods at GIAO-B3LYP/6-311++G(2d.2p) level of theory.[16] FC = Fermi contact term. [c] Experimental data from ref. [14]. [d] This work, sample measured neat at 90 °C. [e] Values referenced to external DMSO at 39.5 ppm. Anion $\delta(^{13}C) = 7.1$ (CH_3). 13.6 (CH_2). 24.6 ppm (CB_{11}). Cation $\delta(^1H) = 0.9$ ppm.

The observed ^{29}Si signal in the NMR spectrum of **2** (δ = 138 ppm) is shifted considerably compared to the resonances observed by ^{29}Si CPMAS NMR spectroscopy of $[Me_3Si][B(C_6F_5)_4]$ (δ = 84.8 ppm)[6] and $[Me_3Si\text{-}H\text{-}SiMe_3][HCB_{11}Cl_{11}]$ (δ = 85.4 and 82.2 ppm)[15] but does not reach the calculated value of δ = 400 pm for the free $[Me_3Si]^+$ cation. For comparison, ^{29}Si chemical shift data for tetramethylsilane (TMS) and trimethylsilyl halides were also computed.[16] These data are consistent with the experimentally observed trends but illustrate that the shielding of the planar coordinated silicon atom in the free cation is characterized by high anisotropy. To model the system as accurately as possible, a HF molecule was attached to the Si center with a Si–F distance of 190 pm, as found in the crystal structure of $[Me_3Si][C_2H_5CB_{11}F_{11}]$ (see below). Even though the structural parameters of the model compound do not change significantly, the computed chemical shift was found to be 200 ppm; the computed anisotropy drops from 469 to 175 ppm.

The $[Me_3Si]^+$ cation seems ideally suited to evaluate the coordination ability of weakly coordinating anions. In silyl cations with bulky mesityl ligands, the interionic interactions are independent of the anion. Thus, the shifts in the ^{29}Si NMR spectra for silyl cations with mesityl ligands with $[B(C_5F_5)_4]^-$[17] and $[HCB_{11}Me_5Br_6]^-$[13] anions in toluene are both around 225 ppm.[6]

The chemical shifts of the Me_3Si group in the ^{1}H and ^{13}C NMR spectra of $[Me_3Si][C_2H_5CB_{11}F_{11}]$ (δ = 0.9 and −2.6 ppm, respectively; the reference signal from the CH_3 group of the anion is found at 1.24 ppm in CD_3CN at room temperature) lie in the expected range for a trimethylsilyl group. However, the relatively small $^1J(^{29}Si^{13}C)$ coupling constant of 53 Hz is surprising. The computational results confirm that this value is dominated by the Fermi contact term, which is smaller in the free cation than in TMS and which is further reduced by a negative paramagnetic spin–orbit term of significant magnitude. In the HF-complexed cation the Fermi contact term is significantly larger, which results in the computed $^1J(^{29}Si^{13}C)$ coupling constant lying between that of TMS and trimethylsilyl chloride, consistent with the experimental data.

The relatively high vapor pressure of the two silyl salts allowed us to obtain single crystals in evacuated vessels at 85 °C (R = H) and 70 °C (R = C_2H_5). Crystals suitable for X-ray diffraction were selected and sealed in fluorolube in a glovebox before being measured at 100 K. The molecular structures of $[Me_3Si][C_2H_5CB_{11}F_{11}]$[18] and $[Me_3Si][HCB_{11}F_{11}]$[19] are shown in Figures 1 and 2, respectively. In both salts the Me_3Si units are coordinated to a *meta*- (relative

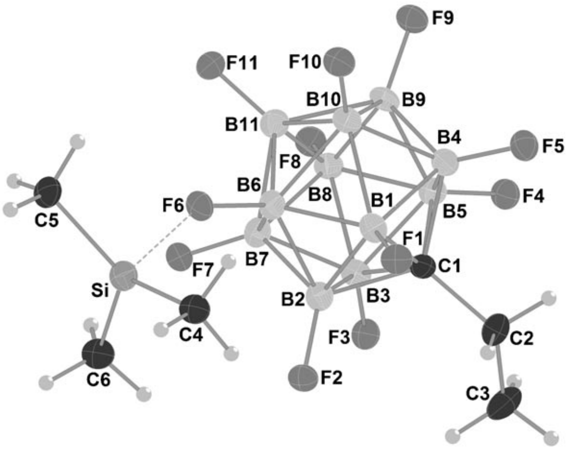

Figure 1. Molecular structure of the asymmetric unit of $[Me_3Si][C_2H_5CB_{11}F_{11}]$. Thermal ellipsoids are set at the 25% probability level.

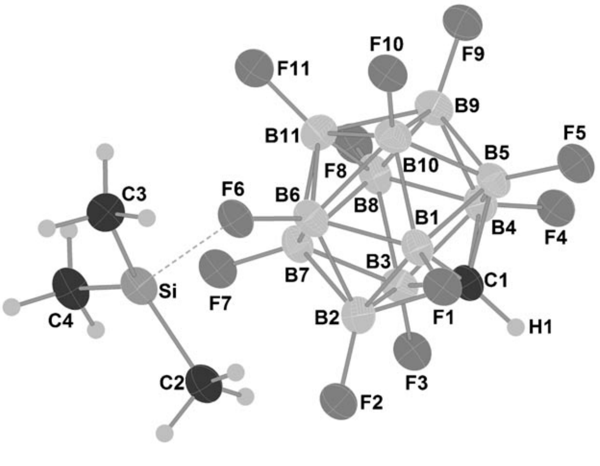

Figure 2. Molecular structure of the asymmetric unit of $[Me_3Si][HCB_{11}F_{11}]$. Thermal ellipsoids are set at the 25% probability level.

to the cluster C atom) fluorine atom, even though the highest electron density should be located at the *para*-fluorine atom of the cluster. This unexpected arrangement is presumably caused by packing effects, since in [iPr$_3$Si][$C_2H_5CB_{11}F_{11}$],[5] the cation is coordinated to a *para*-fluorine atom.

Despite different crystal packing, the bond lengths and angles in the [Me_3Si]$^+$ cations of both salts are almost identical, as shown in Table 2. Even though the [Me_3Si]$^+$ cations in these two salts are not completely planar, the sum of the C-Si-C angles (354.4(3)°) is higher than in other Me_3Si adducts (Table 2). Close examination of the intermolecular contacts reveals that, apart from the short Si···F contacts of 1.878(3) and 1.9001(4) Å, there are longer Si···F contacts between the Me_3Si cation and an adjacent carborane anion on the opposite side (2.922(4) and 2.796(5) Å for [Me_3Si][$C_2H_5CB_{11}F_{11}$] and [Me_3Si][$HCB_{11}F_{11}$], respectively). These second Si···F contacts are considerably shorter than typical distances, which range from 3.2 to 3.6 Å. The sum of the two Si···F contacts for each silyl cation is identical to within 0.1 Å. Moreover, there are F···HCH_2−Si contacts that do not, however, sterically block the central silicon atom. In the carborane cages, the coordinating B−F bonds are on average 0.085(8) and 0.103(6) Å longer than the noncoordinating B−F bonds (1.37(2) and 1.37(1) Å). Such B−F bond elongation is not observed for the second carborane anion on the opposite side, which is located further away from the silyl cation. No distortion of the carborane cages due to the Si···F contacts is observed.

Table 2: Comparison of selected geometric parameters of Me_3Si units in various compounds.

Compound	Sum of C-Si-C angles [°]	Deviation from planarity [Å][a]	Av. Si−C distance [Å]	Si−X distance [Å]	X
[Me_3Si][$HCB_{11}F_{11}$][b]	354.4(3)	0.250	1.821(7)	1.901(4)	F
[Me_3Si][$C_2H_5CB_{11}F_{11}$][b]	354.4(3)	0.253	1.823(5)	1.878(3)	F
[Me_3Si-H-$SiMe_3$] [$HCB_{11}Cl_{11}$][c]	350.1(7)	0.339	1.839(1)	1.62(2)	H
	349.9(6)	0.341	1.838(1)	1.60(2)	H
$Me_3SiNCB(CN)_2F$[d]	349.9(1)	0.341	1.835(2)	1.872(2)	N
Me_3SiF[e]	334.5(2)	0.551	1.848(1)	1.600(1)	F

[a] Distance between the Si atom and the plane defined by the three methyl C atoms in the Me_3Si fragment. [b] This work. [c] Ref. [15]. [d] Ref. [20]. [e] Ref. [21].

Experimental Section

The synthesis of **1** and **2** was accomplished in six or seven steps with various additional purification steps. All reagents and anhydrous solvents were obtained from commercial sources and were used as received. All manipulations were carried out under dry nitrogen (5.0 Air Liquide) using standard Schlenk techniques or in an MBraun glovebox under argon (5.0 Air Liquide; H_2O, $O_2 < 1$ ppm).

Cs[$CB_{11}H_{12}$]: Starting from $BF_3 \cdot OEt_2$ (Fluka; BF_3 content ca. 48%) and $NaBH_4$ (Fluka, ≥98%), [$(CH_3)_3NH$][$B_{11}H_{14}$] (20.0 g, 0.1 mol) was prepared according to the literature method.[22,23] This compound was treated with NaH (29.1 g, 1.21 mol; Fluka, ca. 60%, washed with *n*-pentane before use) in dimethoxyethane (200 mL) at 0°C to afford $Na_2[B_{11}H_{13}]$.[24] After removal of $(CH_3)_3N$ and dimethoxyethane in vacuum, the residue was suspended in dimethoxyethane (400 mL) and treated with $CHCl_3$ (30 mL, 0.37 mol) at 0°C. Subsequently, the mixture was treated carefully with *n*-butanol (125 mL) to give crude Na[$CB_{11}H_{12}$].[24] The crude material was mixed with water (1 L) and the organic phase was removed by rotary evaporation. Addition of $(CH_3)_3N \cdot HCl$ (10.0 g, 0.10 mol; Fluka) precipitated the carborane as the [Me_3NH]$^+$ salt. To remove the unreacted [$B_{11}H_{14}$]$^-$ salt, the [Me_3NH]$^+$ salt was treated with 20% KOH (200 g), and the [$CB_{11}H_{12}$]$^-$ salt was extracted into diethyl ether (3 × 150 mL). Removal of the ether and addition of $(CH_3)_3N \cdot HCl$ with subsequent cation exchange with CsOH (Fluka), drying, and ether extraction afforded pure Cs[$CB_{11}H_{12}$] in 7.6% yield (2.09 g, 7.6 mmol).

Cs[$RCB_{11}F_{11}$] (R = H, C_2H_5): Fluorination of Cs[$CB_{11}H_{12}$] was carried out using a modified literature procedure.[5] Cs[$CB_{11}H_{12}$] (14.4 g, 15 mmol) was treated with anhydrous hydrofluoric acid (25 mL) in a perfluoroalkoxy copolymer (PFA) flask at 45°C for 1 day. The suspension was cooled to −78°C and slowly treated with fluorine gas (Solvay; 0.2 mmol min^{-1}) with vigorous stirring. Once the pressure inside the flask reached 1 bar, the mixture was allowed to warm to room temperature. This procedure was repeated until no more fluorine was absorbed. After removal of any volatile components, the product was taken up in CH_3CN (50 mL), filtered, and the filtrate evaporated to dryness in vacuum. The residue was dissolved in water (200 mL) and treated with $(CH_3)_3N \cdot HCl$ to afford [Me_3NH][$HCB_{11}F_{11}$] in 80% yield (4.80 g, 12.0 mmol). This compound was converted to the Cs$^+$ salt in 60% yield by treatment with two equivalents of aqueous CsOH solution and subsequent ether extraction. Alkylation of Cs[$HCB_{11}F_{11}$] to give Cs[$C_2H_5CB_{11}F_{11}$] was carried out according to a literature procedure[5] with a yield of almost 75%.

[Ph_3C][$RCB_{11}F_{11}$] (R = H, C_2H_5): Cs[$HCB_{11}F_{11}$] (3.23 g, 6.8 mmol) and Ph_3CBr (2.54 g, 7.9 mmol; Aldrich) were weighed in a glovebox into the specially designed filtration apparatus (see Figure S9 in the supporting information). CH_2Cl_2 (30 mL) was condensed into the vessel and the mixture was allowed to stir at room temperature for two days. The mixture was filtered and the residue washed several times with CH_2Cl_2 (30 mL), which was recondensed from the filtrate onto the filter cake. The filtrate was evaporated to dryness and extracted with *n*-pentane (30 mL) to remove the excess Ph_3CBr. Bright yellow [Ph_3C][$HCB_{11}F_{11}$] was thus obtained (1.17 g, 2.0 mmol, 30%). The analogous procedure afforded [Ph_3C][$C_2H_5CB_{11}F_{11}$] in quantitative yield.

[Me_3Si][$RCB_{11}F_{11}$] (R = H (**1**), C_2H_5 (**2**)): The trityl salts described above were treated in the filtration apparatus with 10 mL Me_3SiH. The Ph_3CH was removed by repeated washing with Me_3SiH. Yields were quantitative. Further purification could be achieved by subliming the salts at 110°C under high vacuum ($p < 10^{-2}$mbar).

Crystals suitable for X-ray diffraction were obtained by sublimation in sealed glass tubes. A few milligrams of the compounds were placed into small (6 × 1 mm) glass tubes which were sealed under high vacuum. The sealed tubes were placed in an oil bath at 85°C (R = H) or 70°C (R = C_2H_5) for several days, during which time small, colorless crystals deposited in the cooler parts of the tubes.

H[$RCB_{11}F_{11}$] (R = H, C_2H_5): [Me_3Si][$C_2H_5CB_{11}F_{11}$] (106 mg, 0.24 mmol) was weighed in the glovebox into a tube ($V = 2.5$ mL) fitted with a polytetrafluoroethylene (PTFE) valve (VNMR/10, J. Young).[25] Anhydrous HCl gas (0.8 mmol) was condensed into the tube. After warming to room temperature, a lumpy solid was obtained. After 15 h reaction time, an IR spectrum of the gaseous products was recorded (see Figure S7 in the Supporting Information).

Apart from a small amount of HCl gas, the only other gaseous products were CH_4 and $SiCl_4$ (molar ratio 3:1, confirmed by reference spectrum of a corresponding mixture). The lumpy product could be removed from the walls of the tube by shaking with liquid anhydrous HCl (ca. 0.5 mL) at −55 °C. After some minutes, the HCl was removed in vacuum at −55 °C and the vessel warmed to room temperature, thus giving the product as a fine powder. This substance was treated once again with HCl gas (0.8 mmol) for 5 h at room temperature. After removal of the volatile products, $H[C_2H_5CB_{11}F_{11}]$ (89 mg, 0.24 mmol) was obtained in quantitative yield. $H[HCB_{11}F_{11}]$ was obtained by the analogous procedure starting from $[Me_3Si][HCB_{11}F_{11}]$.

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[18] Crystallographic details for $[(CH_3)_3Si][C_2H_5CB_{11}F_{11}]$ (**2**): $C_6H_{14}B_{11}F_{11}Si$, Bruker AXS Proteum2, $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å), $T = 100$ K, colorless crystals obtained by sublimation at 70 °C, monoclinic, space group $P2_1/c$ (No. 14), $a = 7.384(1)$, $b = 25.491(4)$, $c = 10.037(1)$ Å, $\beta = 110.063(2)°$, $V = 1774.6(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.655\ g\,cm^{-3}$, $\mu(Cu_{K\alpha}) = 2.131\ mm^{-1}$, $F(000) = 872$, 16057 observed reflections ($3.47° \leq \theta \leq 64.71°$), integration with Proteum2/SAINT (V7.23A, 1997–2005 Bruker Analytical X-ray Systems), structure solution by direct methods and refinement on F^2 using 2888 independent reflections (1275 reflections with $I > 2\sigma(I)$) with 262 variables and 0 restraints (SHELXS-97). All non-hydrogen atoms were refined anisotropically. $R1 = 0.0666$ ($I > 2\sigma(I)$).

[19] Crystallographic details for $[(CH_3)_3Si][HCB_{11}F_{11}]$: $C_4H_{10}B_{11}F_{11}Si$, Bruker AXS Proteum2, $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å), $T = 100$ K, colorless crystals obtained by sublimation at 85 °C, monoclinic, space group $P2_1/c$ (No. 14), $a = 11.923(3)$, $b = 7.611(2)$, $c = 17.945(4)$ Å, $\beta = 103.487(2)°$, $V = 1583.6(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.737\ g\,cm^{-3}$, $\mu(Cu_{K\alpha}) = 2.342\ mm^{-1}$, $F(000) = 808$, 14184 observed reflections ($3.81° \leq \theta \leq 65.32°$), integration with Proteum2/SAINT, structure solution by direct methods and refinement on F^2 using 2658 independent reflections (960 reflections with $I > 2\sigma(I)$) with 249 variables and 0 restraints (SHELXS-97). All non-hydrogen atoms were refined anisotropically $R1 = 0.0726$ ($I > 2\sigma(I)$). CCDC 638665 (**2**) and CCDC 638666 (**1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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