



Characterization and Structure of *Trans, Trans, Trans*-1,3,5,7-Tetrakis(3',3',3'-Trifluoropropyl)-1,3,5,7-Tetramethylcyclotetrasiloxane, and Structure of *Trans*-1,3,5-(3',3',3'-Trifluoropropyl)-1,3,5-Trimethylcyclotrisiloxane

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Abstract

One of four possible stereoisomers of a methyl(trifluoropropyl)siloxane cyclic tetramer was isolated from low molecular weight volatiles, formed in a reaction mixture during ring-opening/equilibration polymerization of methyl(3,3,3-trifluoropropyl)cyclotrisiloxane (D_3^F). The crystalline solid was recognized as resembling a previously isolated cyclic siloxane with undetermined stereochemistry, assigned as a cyclotetrasiloxane by IR spectroscopy, and then further characterized by multinuclear (1H , ^{13}C , ^{19}F , and ^{29}Si) NMR spectroscopy as a relatively high symmetry species with respect to the potential *cis–trans* relationships of the methyl and 3,3,3-trifluoropropyl substituents at Si. Unambiguous characterization and assignment of the stereochemistry was accomplished by a single crystal X-ray diffraction study, which revealed the compound was the *trans, trans, trans*-isomer, one species in these equilibration polymerization mixtures. The single crystal X-ray structure of the related, commercially important *trans*- D_3^F cyclotrisiloxane has also been determined. The structures of the two cyclic fluorinated siloxanes are discussed with respect to each other, and in the context of prototypical structures for these common Si_3O_3 and Si_4O_4 ring systems.

Keywords Cyclotetrasiloxane · methyl(3,3,3-trifluoropropyl)siloxane · X-ray structure · Multinuclear NMR of siloxane · CAS # 2374–14-3 · CAS # 429–67-4

1 Introduction

The synthesis of $CF_3CH_2CH_2Si(CH_3)Cl_2$ in 1957 [1], opened the door to production of poly(dialkyl)siloxanes with substituents having vastly different stereo-electronic effects as compared to the poly(dimethyl)siloxane (PDMS) materials commonly produced up to that time. These differences in steric bulk and electronegativity of the substituents at silicon imparted a number of distinct properties to the resultant linear polymers and cross-linked silicone rubbers, such as surface tension [2, 3], density, gas permeability [4], and resistance to swelling in mineral oils and organic solvents [5].

Tarrant produced oligo- and poly[methyl(3,3,3-trifluoropropyl)]siloxanes by hydrolysis of $CF_3CH_2CH_2Si(CH_3)Cl_2$, and isolated discrete, low molecular weight siloxanes formed thereby, in the form of methyl(trifluoropropyl) siloxane cyclic trimer, $[CF_3CH_2CH_2Si(CH_3)O]_3$. Workers at Dow-Corning [6] devised a way to produce the cyclic trimer in commercially useful amounts from the chlorosilane hydrolysis mixture, by cracking the latter in the presence of catalytic KOH, and removing the lowest boiling cyclotrisiloxane via a continuous distillation process [7, 8].

However, other workers pointed out that the trimeric cyclosiloxane distillate described by Pierce, was actually a mixture of two separate compounds with comparable volatility, but slightly different boiling points [9]. Thus, based on physical differences between the components at room temperature, Yuzhelevski et al. were able to separate, purify, and characterize two compounds by fractional crystallization of the neat cyclosiloxane mixture. These researchers proposed that the two compounds with identical elemental composition and

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solution molecular weights were geometric isomers, which differed in the configuration of the 3,3,3-trifluoropropyl substituents with respect to the plane of the 6-membered Si–O ring. Further work based on dipole moment measurements [10], led to structural assignment of the two isomers, with the lower melting point isomer being assigned as the more symmetrical *cis*-isomer, and the room-temperature, crystalline solid denoted as the *trans*-isomer. Later work from this same lab additionally refined the hydrolysate mixture, and fractionally distilled other higher molecular weight cyclic siloxanes, which yielded cuts of isomeric methyl(3,3,3-trifluoropropyl) cyclo-tetra- and pentasiloxanes [11]. The dominant isomeric mixture of cyclotetrasiloxanes isolated by distillation, was fractionally crystallized into three different portions with similar molecular weight, but no specific stereoisomeric assignment was possible nor postulated.

Many years later, Saam and coworkers [12, 13] exploited the earlier discoveries in the methyl(trifluoropropyl)siloxane trimer system and separated out highly purified fractions of both the *cis* and *trans*-D₃^F cyclosiloxanes [14]. Ring opening anionic polymerization of these separate isomers produced linear siloxane polymers, the former of which gave a stereoregular, elastomeric polymer, which exhibited increased tensile strength due to strain crystallization [15, 16]. From this work, it can be seen that polymeric materials with substantially different, improved properties, may be obtained through the use of specific stereoisomeric monomers.

Given the continuing importance of 3,3,3-trifluoropropyl(methyl)siloxane polymeric materials [17, 18] for practical applications in the automotive, aerospace, and medical industries [19], and the recent highlighting of environmental contamination [20–23] by low molecular weight cyclic fluorinated tetrasiloxanes arising from the former's manufacture [24], we report here the isolation of a single isomer of 1,3,5,7-tetramethyl-1,3,5,7-tetrakis(3',3',3'-trifluoropropyl)cyclotetrasiloxane, Compound 1. Multi-nuclear NMR, IR spectroscopic characterization, melting point data, and an unambiguous assignment of its geometry via a single crystal X-ray diffraction study, are presented herein. We also report a single crystal, X-ray structural determination of the closely related *trans* form of 1,3,5-trimethyl-1,3,5-tris(3',3',3'-trifluoropropyl)cyclotrisiloxane, Compound 2 or *trans*-D₃^F, which despite its commercial importance for the production of fluorosilicone materials on a global metric ton-scale over the last 60+ years has never been reported.

2 Experimental

¹H, ¹³C, and ¹⁹F NMR spectra were obtained in acetone-d₆ solvent on a Bruker Avance III HD 600 narrow-bore spectrometer, operating at 600.02, 150.88, and 564.53 MHz, respectively. ¹H-coupled, ¹⁹F NMR spectra were obtained

using the Bruker pulse sequence *zg*, using 16 scans, a 1 s recycle delay, 128 K data points, an acquisition time of 0.3 s, and a spectral width of 400 ppm. The ²⁹Si NMR spectra were obtained in acetone-d₆ solvent on a Bruker Avance III 600 wide-bore spectrometer, operating at 119.27 MHz. The spectra were acquired with inverse gated ¹H-decoupling using the Bruker pulse sequence *zgig*, using 64 scans, a 10 s recycle delay, 64 K data points, an acquisition time of 1.4 s, and a spectral width of 200 ppm. ¹H and ¹³C NMR chemical shifts were referenced to residual proteo-solvent (¹H, δ = 2.05 ppm) and acetone-d₆ (¹³C, δ = 29.84 ppm), respectively [25]. ²⁹Si NMR shifts were referenced to tetramethylsilane (δ = 0.0 ppm), and the ¹⁹F NMR shifts to C₆F₆ (δ = -164.9 ppm) added as internal standards [26].

IR spectra were obtained on neat crystalline solids on a Perkin-Elmer Spectrum 3 FT-IR spectrometer, using a single-bounce universal ATR (attenuated reflectance) accessory with a composite diamond/ZnSe window. Melting point data was measured in glass capillary tubes on a Mel-Temp melting point apparatus. Methyl(3,3,3-trifluoropropyl)cyclotrisiloxane was a mixture of *cis*–*trans* isomers from a commercial source (Thermo-Fisher Scientific, Cat #L16680.14). Solid *trans*-D₃^F and a mixture enriched in the *cis*-D₃^F-isomer (filtrate) were obtained by fractional crystallization from the commercial D₃^F isomer mixture. Hexamethylcyclotrisiloxane (D₃) and octamethylcyclotetrasiloxane (D₄) were obtained from Momentive Performance Materials. Single crystals of *trans*-D₃^F for the X-ray structural study were obtained from the *cis*–*trans* cyclotrisiloxane mixture, by picking out well-formed candidates from the portion which remained solid at room temperature, after having been completely melted at 40 °C, and then slowly cooled from the melt.

2.1 Isolation of (*Trans, Trans, Trans*)-1,3,5,7-Tetramethyl-1,3,5,7-Tetrakis(3',3',3'-Trifluoropropyl)Cyclotetrasiloxane

Vinyl(dimethyl)silyl-terminated, homopolymeric methyl(3,3,3-trifluoropropyl)siloxane was produced by ring-opening polymerization of a commercial mixture of D₃^F (≈75/25% *trans/cis* ratio) with a Na-fluorosilanolate catalyst in the presence of water and 1,3-divinyl-1,1,3,3-tetramethyl disiloxane as chain-stoppers. The polymerization was done on scales ranging from 0.1 to 6.5 kg of D₃^F as starting material. Subsequent silanol condensation and vinyl chain-end equilibration with an excess of linear phosphonitrilic chlorides (LPNC) catalyst, gave a viscous, high MW polymer. In the process of thermally quenching the LPNC catalyst and stripping the 1 kg batch under vacuum (≤200 °C, ≈50 mTorr), a quantity of low molecular weight, D_n^F cyclics, mostly cyclic tetramer, pentamer, and hexamer isomers (n = 4, 5, 6) were obtained as distillate (~200 g). The volatile cyclosiloxanes mixture was filtered through

basic alumina on a glass frit, removing suspended NH_4Cl which sublimed with the overheads, to obtain a clear, colorless fluorosiloxane oil. After sitting at room temperature for 2–3 days, a small amount of fine, white, needle-like crystals spontaneously appeared in the oil, which were isolated by filtration and vacuum drying. Isolated crystalline material was quite small, due to the fact that the crystals of **1** were obtained directly out of the liquid siloxane mixture in which **1** is quite soluble among the congeneric and isomeric siloxanes present that share similar polarity and solubility parameters. Isolated yields from about 200 mg to 2 g of solids were obtained on the 1 kg D_3^{F} polymerization scale, therefore yields of **1** from the distillate mixture ranged from 0.1 to 1% by weight with respect to mass of distillate obtained.

^1H NMR in acetone- d_6 : $\delta(\text{CH}_3)$ 0.270 ppm, s; $\delta(\text{CH}_2\text{CH}_2\text{CF}_3)$ 0.856 ppm, m; $\delta(\text{CH}_2\text{CH}_2\text{CF}_3)$ 2.242 ppm, m – the latter two are 2nd order multiplets due to ^1H - ^1H and ^{19}F - ^1H coupling.

^{13}C { ^1H } NMR in acetone- d_6 : $\delta(\text{CF}_3)$ 128.96 ppm, q ($^1J_{^{13}\text{C}-^{19}\text{F}} = 275.35$ Hz); $\delta(\text{CH}_2\text{CH}_2\text{CF}_3)$ 28.29 ppm, q ($^2J_{^{13}\text{C}-^{19}\text{F}} = 29.87$ Hz); $\delta(\text{CH}_2\text{CH}_2\text{CF}_3)$ 9.39 ppm, q ($^3J_{^{13}\text{C}-^{19}\text{F}} = 2.26$ Hz); $\delta(\text{CH}_3)$ -1.11 ppm, s.

^{29}Si { ^1H } NMR in acetone- d_6 : δSi -20.375 ppm, s.

^{19}F NMR in acetone- d_6 : $\delta(\text{CF}_3)$ -69.539 ppm, t ($^3J_{^{19}\text{F}-^1\text{H}} = 10.91$ Hz).

We also measured the ^{29}Si { ^1H } NMR spectrum of the *cis-trans*- D_3^{F} mixture in acetone- d_6 : $\delta = -9.614$ ppm, s.

Major ATR-FTIR bands for **1** (cm^{-1}): 1446, 1363, 1314, 1261, 1205, 1119, 1061, 1030, 899, 838, 807, 792, 741, 690, and 629.

Melting point for **1**: 73–75 °C.

2.2 X-ray Structural Data Collection and Refinement for *Trans, Trans, Trans*- D_4^{F} ($\text{C}_{16}\text{H}_{28}\text{F}_{12}\text{O}_4\text{Si}_4$, **1**)

A suitable crystal of the Compound **1** (dimensions $0.194 \times 0.058 \times 0.046$ mm³) was selected, attached to a nylon loop, and mounted on a Rigaku XtaLAB Synergy-S Dual-flex diffractometer, equipped with a HyPix 6000-HE HPC detector and a Cryostream 800 low-temperature cryostat. For bond length and angle determinations, the crystal was kept at 100.15 K during data collection which used $\text{CuK}\alpha$ radiation ($\lambda = 1.54184$ Å). Using Olex2 as a GUI [27], the structure was solved with the SHELXT structure solution program by intrinsic phasing [28] and refined with the SHELXL refinement package using least squares minimization [29]. Crystal data are as follows: the unit cell is monoclinic: $a = 16.5807(3)$ Å, $b = 9.8829(2)$ Å, $c = 16.2216(3)$ Å, with $\beta = 91.900(2)^\circ$, and the space group is $\text{C}2/c$. The asymmetric unit consists of half of one molecule (two Si atoms, two oxygen, two methyl groups, and two trifluoropropyl groups) in an all-*trans* (alternating up-down) configuration between

methyl and trifluoropropyl groups on neighboring Si atoms; there are four molecules per unit cell. A total of 19,521 reflections were measured between $10.422^\circ \leq 2\theta \leq 154.106^\circ$, of which 2,734 were unique ($R_{\text{int}} = 0.0334$, $R_s = 0.0206$). The final R_1 was 0.0269 ($I > 2\sigma(I)$) and wR_2 was 0.0734 (all data). There was no disorder to model in any of the trifluoromethyl termini of the trifluoropropyl groups. CCDC 2296541.

2.3 X-ray Structural Data Collection and Refinement for *Trans*- D_3^{F} ($\text{C}_{12}\text{H}_{21}\text{F}_9\text{O}_3\text{Si}_3$, **2**)

A dataset was collected and processed as described above (107.15 K) using a suitable crystal of *trans*- D_3^{F} (dimensions $0.299 \times 0.122 \times 0.078$ mm³). Crystal data are as follows: the unit cell is monoclinic: $a = 9.69800(10)$ Å, $b = 46.1977(5)$ Å, $c = 9.89640(10)$ Å, with $\beta = 113.432(2)^\circ$, and the space group is $\text{P}2_1/c$. A total of 31,782 reflections were measured between $7.654^\circ \leq 2\theta \leq 155.144^\circ$, of which 8,176 were unique ($R_{\text{int}} = 0.0414$, $R_\sigma = 0.0333$). The final R_1 was 0.0310 ($I > 2\sigma(I)$) and wR_2 was 0.0803 (all data). As with the all-*trans* D_4^{F} structure, there was no disorder to model in any of the trifluoromethyl groups. CCDC 2296540.

Major ATR-FTIR bands for **2** (cm^{-1}): 1447, 1421, 1366, 1314, 1263, 1206, 1121, 1064, 1002, 904, 828, 800, 742, 688, 639, and 605.

3 Discussion

Compound **1** was obtained out of a mixture of volatile, low-molecular weight (< 1000 g/mole) cyclosiloxanes, resulting from vacuum stripping of a high molecular weight, vinyl-terminated, linear methyl(3,3,3-trifluoropropyl)siloxane polymer. The distribution of cyclic methyl(3,3,3-trifluoropropyl)siloxanes in equilibrium with linear homopolymer, contains a majority of cyclic siloxane species, and of these, dominantly the cyclic tetramers, pentamers and hexamers. A typical distribution (wt%) comprises 41–47% D_4^{F} , 31–36% D_5^{F} , and 7–8% D_6^{F} isomers, with only 13–17% linear polymer [30]. Further, in the most volatile portion, obtained by distillation under reduced pressure, the cyclic tetramer siloxanes make up an even greater proportion of the mixture. Yuzhel-evskii reported distillable fractions from a caustic hydrolytic polymerization mixture as containing $\approx 16\%$ trimers, 75% tetramers, and 9% pentamers [11].

However, given the presence of multiple cyclosiloxane oligomers even in the distillate (with molecular weights varying from 625–937 g/mole), plus the possibility of numerous stereoisomeric forms for each given formula weight which could broaden or depress the melting points of the other individual components, the likelihood of resolving any one specific compound appeared slim. It is therefore *surprising*

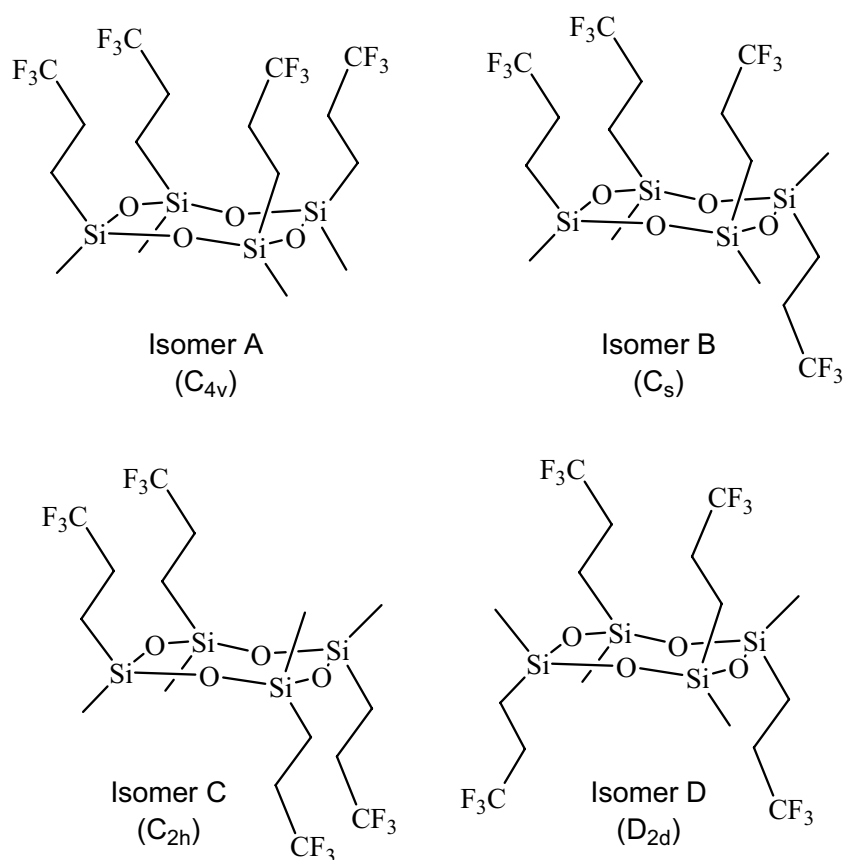
that a solid, crystalline precipitate was observed to form from such a complex mixture, where all the congeneric and isomeric siloxanes share a common repeat unit, have similar polarity and solubility parameters, and also likely have a high mutual solubility in one another. Based on the dominant cyclosiloxane oligomer in both the polymerization reaction and the resultant distillate mixture, on a mass basis alone it was likely that the solid material which crystallized out was a cyclotetrasiloxane.

Workers at Dow-Corning first revealed significant differences in Si–O stretching frequencies between various cyclic diorganosiloxane oligomers, that could be used to identify families of specific isomers based on Si–O ring sizes [31]. It was subsequently more generally found that both symmetric $[R_2SiO]_x$ and asymmetric $[RR'SiO]_x$ diorganosubstituted cyclosiloxanes, possessed strong asymmetric Si–O stretching frequencies of the siloxane rings which fell into specific ranges for cyclic trimers ($x=3$) and for cyclic tetramers ($x=4$) [32]. Thus, on the basis of that work, the vibrational spectrum of crystalline solid **1**, was examined. A strong absorption at 1030 cm^{-1} was seen in the IR spectrum, which was taken as indicative of a cyclotetrasiloxane ring in comparison to the mixture of $[CF_3C_2H_4(CH_3)SiO]_3$ isomers, as well as D_3 and D_4 reference samples [33]. A difference in

wavenumber position was observed for the Si–O–Si stretch dependent on spectral acquisition mode, whether by transmission as a solution or neat liquid or by attenuated reflectance as a pure solid or neat liquid (see Supplementary Information (SI), Figs. S6–S10 and Table S1). Knowing now that the isolated solid material was very likely a tetrasiloxane, it then remained to identify which geometric cyclotetrasiloxane Isomer A–D corresponded to Compound **1**.

In the family of D_4^F cyclosiloxanes, there are 4 possible stereoisomers, denoted A–D in Fig. 1 below [34]. Isomer A is the all-*cis* molecule, where all of the trifluoropropyl groups lie on the same side of the Si_4O_4 ring (all $-C_2H_4CF_3$ up or down). Isomer B has the arrangement with three trifluoropropyl groups on the same side of the ring, and the fourth one oriented in the opposite direction (three trifluoropropyls up and one down; *cis-cis-trans*). Isomers C and D both have two $CF_3C_2H_4-$ groups on one side of the ring and the other two trifluoropropyl groups on the opposite side. Isomer C is the cyclic siloxane variant where the same-side-oriented trifluoropropyl groups are on adjacent Si atoms (two fluoropropyl groups up and two down; *cis-trans-cis* orientation); Isomer D is similar, except the same-side oriented trifluoroalkyl groups are on Si atoms located across from each other on the Si–O ring and the orientation of the

Fig. 1 Graphical representation of the four possible D_4^F stereochemical isomers and approximate point group symmetry of each molecule



substituents are alternately above and then below the Si–O ring (two trifluoropropyl groups up and two down; *trans, trans, trans* – or “all-*trans*” isomer).

In the process of chain growth by condensation of an unsymmetric diorganosilane diol (alternatively, formation of cyclic oligomers by cycloreversion in an equilibration polymerization), the arrangement of each siloxane repeat unit with respect to the successive one in a sequence gives rise to the possibility of stereoisomers. Assuming random probability of a given incoming methyl(trifluoropropyl) siloxane unit being in any specific orientation with respect to the first one, and little if any energetic difference in the orientation of a successive unit being added, one can calculate *reasonable* cyclic isomer probability distributions, based solely on the cumulative probabilities [35, 36]. From these considerations, the relative abundance of the four isomers A to D as indicated above, should be in the ratio 1:4:2:1, respectively.

Cai and co-workers observed four such isomers in reference mixtures of D_4^F (and also in environmental samples), which were separated by gas chromatography and in all fractions, their molecular weights each corresponding to $[CF_3C_2H_4(CH_3)SiO]_4$ were verified by a mass-selective detector [37]. They were not able to directly determine the stereochemistry using GC–MS data alone. However, the authors assigned stereochemistry for each cyclotetrasiloxane component in the mixture, using the relative signal intensity in the total ion chromatogram, which qualitatively matched the expected 1:4:2:1 molar ratio derived from purely random statistical considerations. Accordingly in order of increasing retention time, t_r , the separated isomeric, D_4^F cyclic siloxanes were assigned as $t_r = 12.027$ min = (*cis, cis, cis*) Isomer A; $t_r = 12.496$ min = (*cis, cis, trans*) Isomer B; $t_r = 12.643$ min = (*cis, trans, cis*) Isomer C; and $t_r = 12.827$ min = (*trans, trans, trans*) Isomer D. This work established proof that all four possible D_4^F isomers can be formed in industrial polymerization processes, and that their amounts followed a predicted distribution. However, insufficiently small quantities were separated for additional study, further details about other spectroscopic and physical properties of each separated isomer were not investigated, and more direct confirmation of the assigned stereochemistry was still lacking.

Before turning to more detailed spectroscopic investigations, we note that the observed melting point of Compound **1** isolated in this work was 73–75 °C, which fairly closely matches the 76.5–77 °C value for a room-temperature solid fraction, denoted as “Substance 1” by Yuzhelevski [11]. Substance 1 was the highest melting point compound isolated from a distillate cut containing tetrasiloxane isomeric materials $[CF_3C_2H_4(CH_3)SiO]_4$ (characterized by its solution molecular weight). We therefore believe Compound **1** (this work) likely corresponds to Substance 1 from earlier work. One could rationalize that in the solid state, Substance

1 and Compound **1** here, based on their high melting points, might represent the most densely packable arrangement of the four isomeric cyclotetrasiloxanes A–D. However, which of these four stereoisomers would pack the most efficiently is not intuitively obvious, as it is not always the case that the most symmetric isomer packs more densely in the solid state and/or retains its solid structure to a higher temperature. As an example, the higher melting form of the related cyclic trimer, *trans*- D_3^F has nominally C_3 point group symmetry, while the lower melting point, *cis*- D_3^F isomer belongs to the much higher symmetry, C_{3v} point group class. In contrast, in the methyl(phenyl)cyclotrisiloxane system, the higher symmetry *cis*- $[CH_3(C_6H_5)SiO]_3$ has a melting point of ≈ 100 °C, while the lower symmetry *trans*- $[CH_3(C_6H_5)SiO]_3$ melts at 40 °C [34].

We next turned to NMR spectroscopy to further characterize Compound **1** and differentiate it amongst the possible Isomers A–D, based on spectra obtained for the 1H , ^{13}C , ^{29}Si , and ^{19}F nuclei present. In contrast to the commercially important D_3^F cyclotrisiloxanes, for which both pure isomeric forms have been isolated and 1H , ^{13}C , ^{29}Si , and ^{19}F NMR data tabulated [38–42], much less information on the congeneric D_4^F cyclotetrasiloxanes is known. The 1H NMR of **1** shows a singlet Si– CH_3 resonance ($\delta = 0.270$ ppm), as well as only two sets of multiplet resonances associated with the $-C_2H_4-$ portion of the 3,3,3-trifluoropropyl group, bearing coupling to ^{19}F of the terminal $-CF_3$ group (see Supplementary Information (SI), Fig. S1). Kalig and coworkers [41] found only three resolvable Si– CH_3 peaks in the range 0.23 to 0.25 ppm in a commercial reference mixture of D_4^F isomers, and tentatively assigned other species at 0.26 and 0.28 ppm as arising from the higher molecular weight homologs D_5^F and D_6^F of undefined stereochemistry [43].

The peak assignments in the ^{13}C NMR for the $-CH_3$, and C1, C2, and C3 of the 3,3,3-trifluoropropyl groups in **1** were first made on the assumption of: 1) the Si– CH_3 chemical shift being the closest to the TMS reference, and 2) then going downfield for the trifluoropropyl carbons C1–C3 in that order, the latter being less shielded by their increasing proximity to the highly electron-withdrawing, terminal $-CF_3$ group (see SI, Fig. S2). The ^{13}C -NMR chemical shift peak assignments were confirmed through the use of an 1H - ^{13}C HSQC experiment (see SI, Fig. S3). Finally, the assignments were in accord with the expectation that the ^{13}C - ^{19}F coupling constants would increase in the order $^1J_{13C-19F} > ^2J_{13C-19F} > ^3J_{13C-19F}$, with the observed chemical shifts/coupling constants being C1 (9.39 ppm, 2.26 Hz), C2 (28.29 ppm, 29.87 Hz), and C3 (128.96 ppm, 275.35 Hz). We note in passing that the ^{13}C NMR spectrum observed here for Compound **1**, and those reported for both *cis*- and *trans*- D_3^F [41], showed ^{13}C - ^{19}F coupling to all three carbons of the trifluoropropyl groups, which was of comparable magnitude in both sets of siloxanes.

Yuzhelevskii et al. attempted empirical, group contribution additivity calculations, based on perturbation of the ^{29}Si NMR chemical shift relative to the parent all-methyl siloxanes, in a series of mixed $\text{D}_x\text{D}_y^{\text{F}}$ cyclics ($x + y = 3, 4, 5$), but the agreement between calculated and observed chemical shifts for the D_4^{F} isomers was not very good [38]. They further expected that with six potentially stereochemically different Si environments in the four possible D_4^{F} stereoisomers, there might be only five distinct chemical shifts seen, because of the similarity in calculated resonance values for Isomers C and D. In reality, these workers observed just two resolved peaks in the experimental ^{29}Si spectrum of a D_4^{F} mixture, at -19.84 and -20.06 ppm [44]. Other researchers observed two separate resonance envelopes, each one consisting of at least two partially overlapping single peaks, at approximately -20.1 and -20.3 ppm [42]. The ^{29}Si -NMR spectrum of Compound **1**, which showed only a single resonance at -20.38 ppm, corresponds well with the more upfield resonance of this latter work (see SI, Fig. S5). As with other researchers who had previously examined the *cis*- or *trans*- D_3^{F} compounds (or a mixture thereof) by ^{29}Si -NMR [38, 40–42], it is noteworthy to elaborate that we were also unable to either resolve separate signals for the two types of inequivalent Si atoms in *trans*- D_3^{F} , or to observe different chemical shifts attributable to the two stereoisomers, in a *cis*-*trans*- D_3^{F} mixture. Even when measured at higher magnetic field than in previous work (14.1 T vs $9.4, 7.0, \text{ or } 2.35$ T), we still observed only a single, unresolved resonance at -9.61 ppm for all Si-atoms in the *cis*-*trans*- D_3^{F} isomer mixture.

Finally, it has been evident in work on the stereoregularity of linear siloxane polymers prepared from *cis*- D_3^{F} [12], that ^{19}F NMR has the highest sensitivity and ability to discriminate subtle polymer microstructure and tacticity resulting from the combination of methyl and 3,3,3-trifluoropropyl groups on each Si atom. Examination of a reference mixture of D_4^{F} isomers by ^{19}F NMR [41], showed good resolution of five distinct single peaks spanning a narrow range of <0.1 ppm around -69.77 ppm. We observed a single ^{19}F NMR resonance for the $-\text{CF}_3$ group in **1**, split by geminal ^{19}F - ^1H coupling to the adjacent methylene, at -69.53 ppm, which is slightly downfield of all the peaks in the reported D_4^{F} isomer mixture (see SI, Fig. S4). From the totality of our NMR data, all of the spectra for **1** are relatively simple, and show an apparent single environment for the $-\text{[CF}_3\text{C}_2\text{H}_4(\text{CH}_3)\text{SiO]}-$ unit and its methyl/fluoroalkyl group sub-components. Accordingly, the structures of Isomer A, C, or D would be consistent with the observed spectra, and only Isomer B might be ruled out by its magnetically inequivalent alkyl groups [45]. Assignment of the stereochemistry of **1**, therefore necessitated the use of a single crystal X-ray diffraction study for a definitive result.

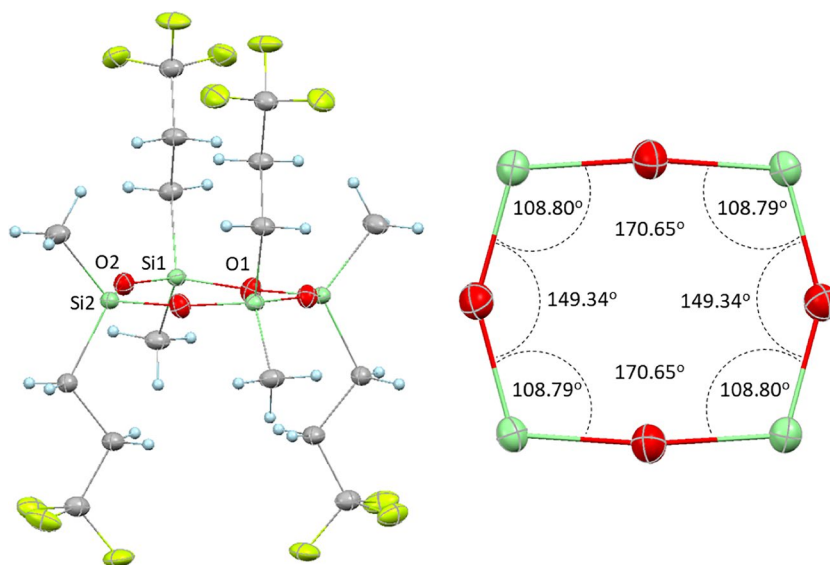
4 X-Ray Structural Studies

For small ring size, dialkyl cyclosiloxanes containing the specific methyl(3,3,3-trifluoropropyl) siloxane repeat unit, *no definitive structural data have been determined*. However, You et al. investigated the thermal decomposition of HO- and $(\text{CH}_3)_3\text{SiO}$ -terminated fluorosilicone polymers, and in explaining the behavior of these materials, optimized the geometry of the all-*cis* isomers of both D_3^{F} and D_4^{F} by ab initio calculations [46]. Therefore, the directly measured X-ray structural data results presented here for *trans*- D_3^{F} and *trans,trans,trans*- D_4^{F} give an opportunity to gauge the fidelity of the computational results in reproducing at least the major features of Si–O bond lengths and angles in these 6- and 8-membered cyclosiloxanes.

4.1 Structural Details of Compound 1

The averaged bond lengths and angles of *all-trans*- D_4^{F} (**1**) are Si–O = $1.623(6)$ Å, Si–C = $1.855(9)$ Å, $\angle\text{O-Si-O} = 108.795(6)^\circ$, and $\angle\text{C-Si-C} = 111.300(12)^\circ$. Bond lengths determined for **1** are in agreement with those seen previously for cyclic tetrasiloxanes; this includes the closest related compound octamethylcyclo-tetrasiloxane that averaged showed Si–O = $1.650(25)$ Å and Si–C = $1.92(7)$ Å [47], with values for the O–Si–O and C–Si–C angles that approach an idealized tetrahedral angle. Distances between Si centers related by symmetry in the ring of D_4^{F} measure 4.499 Å and the shortest Si–Si distance (nearest neighbor) is 3.145 Å. Unlike puckered conformations reported for [(biphenyl-2-yl) $_2\text{SiOSiMe}_2\text{O}$] $_2$ [48], [(phenyl) $_2\text{SiOSiMe}_2\text{O}$] $_2$ [49, 50], [(C $_6\text{H}_5$) $_2\text{SiO}$] $_4$ [51], and [(CH $_3$) $_2\text{SiO}$] $_4$ [47] tetramers, the siloxane ring of D_4^{F} is nearly planar (Fig. 2) as seen in conformationally related tetramers, namely [CH $_2\text{F}(\text{CH}_3)\text{SiO}$] $_4$ [52], [OCN(CH $_3$)SiO] $_4$ [53], [$^t\text{Bu}_2\text{SiOSiMe}_2\text{O}$] $_2$ [54], [(^tBu)FSiO] $_4$ [55], and [(C $_6\text{H}_5$) $_2\text{SiO}$] $_4$ [51, 56–59]. Two intersecting planes defined by Si2 O2 Si1 O1 Si2' and Si2 O1' Si1' O2' Si2' form an angle of 8.3° , and the fourth Si atom not part of either plane defined by the other three Si atoms is only displaced from the Si $_3\text{O}_2$ r.m.s. plane by 0.321 Å (Fig. 2 shows deviation of all ring atoms from planarity). The configuration of an eight-membered Si $_4\text{O}_4$ cycle directly depends on the values of Si–O–Si angles, which for this isomer feature strongly different Si–O–Si endocyclic angle values with 149.34° and 170.65° (Fig. 2). These $\angle\text{Si-O-Si}$ angles are *very different* from angles determined by quantum chemistry calculations at the DFT-B3LYP level and represent a key feature of **1** which is not typical of other cyclic tetramers. A minimum energy (optimized geometrical) structure of *all-cis*- D_4^{F} (Isomer A) exhibited

Fig. 2 *Left:* ORTEP drawing of *trans, trans, trans*-D₄^F (**1**) that is nearly planar. Thermal ellipsoids are drawn at the 50% probability level. Light green: silicon; red: oxygen; yellow: fluorine; gray: carbon; light blue: hydrogen atoms. *Right:* Top-down view of the Si₄O₄ ring and interior angles therein



Si–O–Si bond angles that more narrowly span from 137.1° to 146.3°. Differences between Si–O bond lengths in D₄^F that were calculated (1.6570 Å, σ = 0.0044 Å) [46] and experimentally determined (1.6234 Å, σ = 0.0062 Å, this work) are otherwise unremarkable, but they are in fact statistically significantly different.

4.2 Structural Details of Compound 2

We also determined the crystal structure of the more abundant, *trans*-isomer of the related cyclic trimer **2**, *trans*-D₃^F, which is shown in Fig. 3. A minimum energy structure calculated for *cis*-D₃^F showed a Si–O bond length of 1.6663(33) Å [46] that does not agree with the experimentally determined shortened length of 1.6432(29) Å (this work). A calculated Si–O–Si bond angle of 132.0(7)° agrees [46] with the experimentally determined value of 131.9(12)° (this work). While crystal structure determinations of numerous and varied cyclotrisiloxanes have been reported [60–62], to our knowledge no *fluorinated alkyl derivatives have appeared in the literature*. The average Si–O distance we report here for **2** is similar to other cyclotrisiloxanes with organic functional groups, and both Si–O–Si and O–Si–O bond angles also compare favorably with other known organic containing cyclotrisiloxanes. The Si₃O₃ ring of *trans*-D₃^F is not planar among Si₃O₃ ring structures; O3 is located 0.163 Å and O2 is 0.217 Å above a plane defined by the three silicon atoms, while O1 is 0.063 Å out of the plane. Similar deviation from planarity (*albeit* smaller) was reported for [(tBu)phenylSiO]₃ [55] that featured two of three oxygen atoms 0.142 Å above the plane defined by three silicon atoms. Typically, Si₃O₃ ring structures are essentially planar [61], as in [((vinyl)methylSiO(phenyl₂SiO)₂)] [60], with an average deviation of 0.0506 Å from planarity for the atoms of the ring.

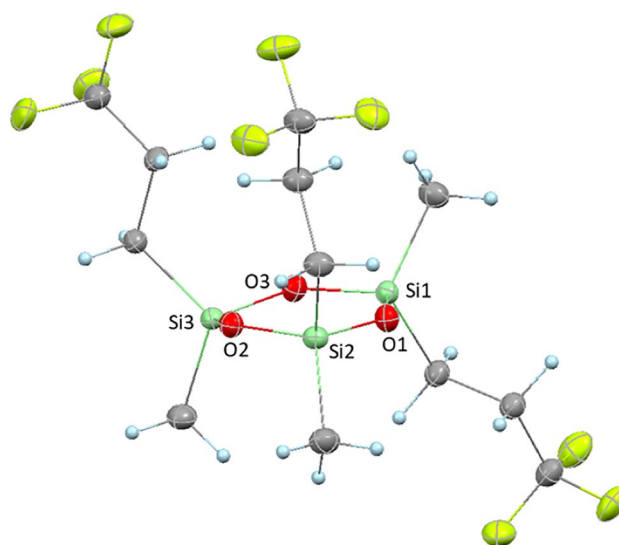


Fig. 3 ORTEP drawing of *trans*-D₃^F (**2**). The Si₃O₃ ring is not planar. Thermal ellipsoids are drawn at the 50% probability level. Light green: silicon; red: oxygen; yellow: fluorine; gray: carbon; light blue: hydrogen atoms

5 Conclusion

Stereoisomers of D₃ and D₄ fluoropropylcyclosiloxanes of industrial and environmental importance, previously described only in mixtures with other isomers, were isolated and characterized spectroscopically as well as by single crystal structure analysis. X-ray structural data results for *trans,trans,trans*-D₄^F (**1**) and *trans*-D₃^F (**2**) gave an opportunity to gauge the fidelity of computational results. \angle Si–O–Si angles in **1** are very different from angles determined by calculations at the DFT-B3LYP level and

represent a key feature of **1**. While for **2**, an experimentally determined Si–O bond length does not agree with a calculated (elongated) Si–O bond length from a minimum energy structure calculated for **2**.

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Data Availability The data generated and/or analyzed during the current study are available from the corresponding author on reasonable request, but please read the supplementary information of this article prior to any request. Crystallographic data for **1** and **2** in this article have been deposited at the Cambridge Crystallographic Data Centre, under numbers CCDC 2296541 (**1**) and 2296540 (**2**). Copies of the data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>. All other data generated and analyzed during this study, which include experimental and spectroscopic data, are included in this article and its supplementary information.

Declarations

Ethics Approval The authors declare that there were no ethical issues during this research.

Consent to Participate All the authors consent to participate in this research.

Consent to Publication All the authors consent to the publication of this research.

Competing Interests The authors declare no competing interests.

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 44. It should be noted that in the ^{29}Si NMR experimental data cited, the spectra were measured on a low-field (100 MHz ^1H -resonance frequency, ≈ 2.35 Tesla field strength) instrument, which may have limited resolution of all the isomers present. The spectra were also acquired in CCl_4 , which might obviate direct comparison of chemical shift data with this work (in acetone- d_6) due to solvent-effects
 45. In reality, symmetry inequivalent atoms in a structure may not be present in sufficiently different magnetic environments to be resolved in the NMR spectrum as observable chemical shift differences or specific spin-spin splittings dictated by that inequivalence. As an example, the 75 MHz ^{29}Si -NMR spectrum of the commercial *cis*- and *trans*- D_3^{F} mixture, with three different Si-methyl or 3,3,3-trifluoropropyl group environments, was not resolvable into distinct resonances for the two isomeric forms, much less distinguishing the two equivalent ring sub-units from the third one in the *trans*-isomer. See Ref. 33
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