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In situ crystallization of 2,2-dimethoxypropane and dimethyldimethoxysilane: hunting for Group 14 isomorphism

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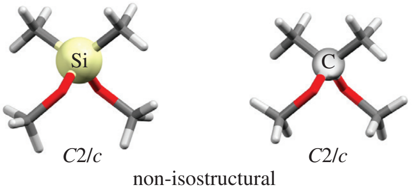
Two closely related 2,2-dimethoxypropane and dimethyldimethoxysilane liquids were *in situ* crystallized, and their crystal structures were determined by single-crystal X-ray diffraction analysis. Qualitative and quantitative differences in the crystal packing are discussed.



Isomorphism is a well-known phenomenon, which is common for inorganic materials and not unusual for molecular crystals built from molecules of the same shape. For instance, there are numerous isostructural coordination complexes of Ni / Pt / Pd, other transition metals, and lanthanides.[1] At the same time, systematic studies of the influence of the atomic radii of main group elements on crystal packings are scarce, although the understanding of isomorphism and isostructurality can be helpful in constructing new crystalline materials.[2–4] The main problem of such studies is that the crystal packing of closely related compounds can be affected by the substituted atoms or groups, *e.g.*, by the presence of active lone electron pairs or flexible substituents; thus, even an insignificant change in molecular composition leads to a different crystal structure instead of an isostructural crystal. Therefore, to exclude these factors in a study of possible isomorphism, it is desirable to use small rigid molecules where diverse atoms (or groups of atoms) do not participate in strong intermolecular interactions.

For the above reason, we have chosen two small organic molecules of dimethyldimethoxysilane **1Si** and 2,2-dimethoxypropane **1C**. These compounds differ only in the central tertiary atoms, which are screened by connected methyl and ether groups and cannot participate in strong intermolecular interactions. **1Si** was synthesized according to a published procedure[5] and purified by distillation, and commercial **1C** from Sigma-Aldrich was used without further purification.

Both of the compounds are liquid at room temperature, and *in situ* crystallization was used to obtain crystalline samples suitable for X-ray structure determination. Crystallization was performed using a Lindemann glass capillary of 30 mm long and 0.3 mm in diameter, which was filled with a substance, sealed by flame, and mounted on a Bruker Smart Apex II diffractometer equipped with an Oxford Cryostream cooling device. The capillaries were aligned with a direction of nitrogen flow to minimize temperature non-uniformity caused by turbulence. The samples were slowly cooled to temperatures 30–40 K lower than T_m (193 K for **1Si** or 226 K for **1C**) with the formation of glassy and/or heavily polycrystalline materials. Then, a zone melting technique was used by spot heating with a nichrome wire heater moving along the capillary at a constant speed. The melting/solidification process was repeated until a diffraction pattern quality becames suitable for indexing and integration. Finally, the temperature was lowered to 120 K, and data collection was performed by one ω and one φ-scan allowed by a restricted geometry set-up. Note that, in both cases, the final samples still contained multiple crystals, and frame integration was performed for up to three crystals at the same time (for **1C** at 218 K, for details see Online Supplementary Materials).

Despite the apparent similarities of the two molecules, their crystals[†] are not isostructural, though share some common features. Both structures belong to space group $C2/c$, and molecules lie in a crystallographic two-fold axis.

Conformations of the two molecules coincide (Figure 1): in both crystals, the O(3)–C(4) bond is virtually collinear to the X(1)–C(2) bond with the C(2)–X(1)–O(3)–C(4) torsion angles of 176.41(11) and 179.20(16)° for X = Si and X = C, respectively. The observed conformation is apparently defined by stereoelectronic effects that can be described in terms of the second-order perturbation analysis of a Fock matrix in a natural bond orbital (NBO) basis[6] as a stabilizing interaction of lone pairs of electrons of oxygen atoms and antibonding orbitals of X–C and X–O bonds. The refined orientations of the terminal methyl groups are also very close in both structures. Bond lengths and angles in two structures are typical of the corresponding fragments of the related compounds (see Online Supplementary Materials). In the context of structure similarity,

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[†] *Crystallographic data for* **1Si** ($C_4H_{12}O_2Si$). At 120 K colorless crystals are monoclinic, space group $C2/c$, a = 11.788(7), b = 10.0768(6) and c = 8.3937(9) Å, β = 131.6270(10)°, V = 745.3(5) Å^3, Z = 4 (Z' = 0.5), d_{calc} = 1.071 g cm^{-3}; 3675 reflections measured ($2\theta < 60°$), 966 reflections independent (R_{int} = 0.0176); R_1 = 0.0297 [for 913 reflections with $I > 2\sigma(I)$], wR_2 = 0.0877, GOF = 1.044.

Crystallographic data for **1C** ($C_5H_{12}O_2$). At 120 K colorless crystals are monoclinic, space group $C2/c$, a = 10.7198(16), b = 6.3871(10) and c = 9.6730(14) Å, β = 105.873(5)°, V = 637.04(17) Å^3, Z = 4 (Z' = 0.5), d_{calc} = 1.086 g cm^{-3}; 4827 reflections measured ($2\theta < 60°$), 874 reflections independent (R_{int} = 0.0767); R_1 = 0.0709 [for 627 reflections with $I > 2\sigma(I)$], wR_2 = 0.1876, GOF = 1.021.

Additional details on crystal structure determination, including data for **1C** at 218 K (not discussed in the paper) can be found in Online Supplementary Materials.

CCDC 1903036–1903038 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

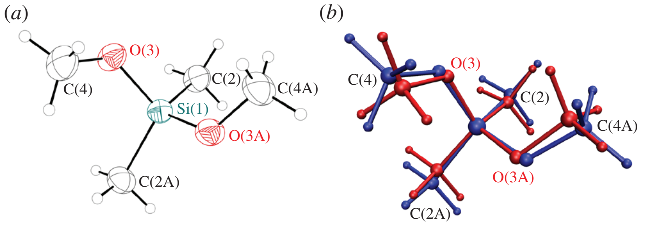
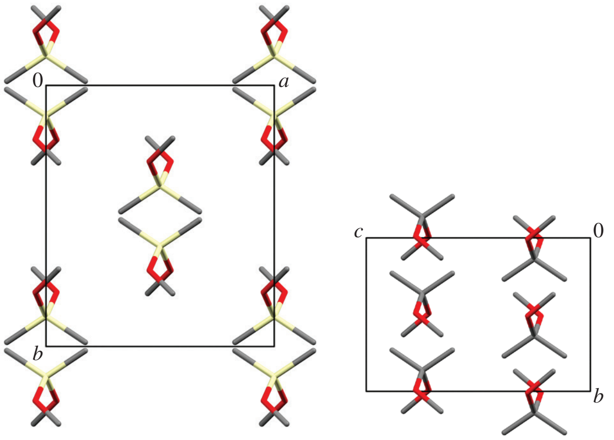


Figure 1 (*a*) General view of the molecule of **1Si** in a crystal in a thermal ellipsoid representation ($p = 50\%$). (*b*) Overlay of the molecules of **1Si** (blue) and **1C** (red), the best fit of the labeled atoms.

important difference is between the pairs of X–C and X–O distances [X = Si: Si(1)–C(2) 1.8468(16), Si(1)–O(3) 1.6391(9) Å, X = C: C(1)–C(2) 1.521(2), C(1)–O(3) 1.424(2) Å].

Although the molecular conformations are very similar, a simple visual inspection shows that the crystal packings in two molecules are different (Figure 2). It is reasonable to assume that the volume of a molecule and its surface area accessible for intermolecular interactions are higher in the case of a Si analogue due to longer Si–O and Si–C bonds. Indeed, molecular volumes defined by unit cells are 186.3(2) and 159.6(5) Å^3 for **1Si** and **1C**, respectively, at 120 K with a difference of about 27 Å^3. This relatively high value originated from a difference between the covalent radii of Si and C atoms (1.11 and 0.76 Å, repectively)[7] since the volume of a spherical molecule is proportional to the cube of its radius. The molecular surface accessible to intermolecular interactions in a crystal can be estimated, for instance, with the Hirshfeld partitioning scheme.[8] The areas of Hirshfeld surfaces (HSs) calculated for experimental geometries (with C–H of 1.083 Å) are 188.0 and 159.4 Å^2. Note that, despite a difference in the volumes and areas, the surfaces are built by the same set of atoms since the central atom X (Si or C) is shielded by the substituents. Moreover, the quantitative analysis of HS[9,10] shows that, in both cases, H···H contacts dominate in crystal packing: 82.7% (155.4 Å^2) in **1Si** and 83.8% (133.55 Å^2) in **1C** of the surface area correspond to this type of the contacts. The remaining 17.3% (32.6 Å^2) in **1Si** and 16.2% (25.8 Å^2) in **1C** come from C–H···O contacts.

Due to the absence of directed and strong intermolecular interactions, it is difficult to rationalize differences in the crystal packings. Therefore, *ab initio* calculations were used to estimate energetic characteristics of the two crystal structures. The calculations were performed within a DFT approach with PBE0-D3[11,12] functional and atom-centered basis set POB-TZVP[13] with the CRYSTAL17 program[14] (see Online Supplementary Materials for details). Full geometry optimization of the atomic coordinates and unit cell parameters for crystal structures and geometry optimization of isolated molecules were performed to obtain packing energies. For comparison, crystal structures were also optimized using experimental unit cell parameters since the DFT approach has a well-known problem with unit cell optimizations (Table 1). In the following, we distinguish the lattice energy E_{latt}, the energy difference between the crystal and isolated molecule frozen in crystal geometry, and E_{form}, the energy difference between optimized crystal and isolated structures; both quantities being corrected for a basis set superposition error (BSSE), and the latter for the energy of zero-point vibrations (ZPE).



1Si **1C**

Figure 2 Fragments of the crystal packing of **1Si** (view along *c* axis) and **1C** (view along *a* axis).

The DFT approach adequately reproduces the experimental geometry of molecules (see Online Supplementary Materials). The molecular geometry is almost the same in an isolated state, and the modest differences are a bit more pronounced for **1Si** with a deformation energy of 0.8 kcal mol^{-1}, while in case of **1C** these two quantities differ at most by 0.2 kcal mol^{-1}.

Without unit cell optimization, the E_{latt} of **1Si** is by 2.1 kcal mol^{-1} higher than that for **1C**, and the calculated difference in E_{form} is 1.4 kcal mol^{-1} with a deformation energy and ZPE correction. Note that, despite a significant shrinkage of the unit cell volume, the optimization of unit cell parameters leaves these differences almost unchanged: $\Delta E_{\text{latt}} = 2.0$ kcal mol^{-1} and $\Delta E_{\text{form}} = 1.3$ kcal mol^{-1}. The apparent lowering of the E_{form} by unit cell optimization is only due to an increase in ZPE energy.

It was interesting to calculate the energetic characteristics of crystals with isomorphous substitution, *i.e.*, if the packing pattern of **1C** is used for **1Si** and *vice versa*. For this purpose, we performed a full geometry optimization of such model structures further denoted as **1Si**[1C] and **1C**[1Si]. If we use the packing pattern of a heteroanalogue, the unit cell parameters should adjust the molecular size and shape. The unit cell should be shrunk or expanded in the case of **1C**[1Si] or **1Si**[1C], respectively. This is actually that we see after optimization, but the resulting volumes are higher than those in real structures; therefore, a packing pattern of the heteroanalogue is non-optimal in the context of the principle of close packing (see Table 1). The values of E_{latt} and E_{form} also indicate that **1C**[1Si] and **1Si**[1C] are less favorable than the experimental crystal structures. It should be noted that, in case of **1Si**[1C], the E_{form} difference with **1Si** is only 0.4 kcal mol^{-1}, which is a typical, energy difference of polymorphic modifications.[15] On the other hand, **1C**[1Si] is significantly (by 1.5 kcal mol^{-1}) less favorable than the experimental structure.

In the absence of specific interactions, given the approximately equal ratios of interactions of different types for the two compounds, one can suppose that a positive correlation exists between the surface area and the energy of interactions, or even an energy-to-surface ratio is constant. The ratios calculated from the above data (see Table 1) support this assumption for experimentally determined

Table 1 Lattice and formation energies, molecular volumes, molecular HS areas and lattice energy/HS area ratios for the crystals of **1Si** and **1C**.

Data source	E_{latt}/ kcal mol^{-1}	E_{form}/ kcal mol^{-1}	Volume/Å^3	HS area/Å^2	E_{latt} HS^{-1}/ kcal mol^{-1} Å^{-2}
			1Si		
exp.	15.9	14.5	181.5	188.0	0.0846
DFT	16.1	13.8	157.2	172.8	0.0932
DTF in [1C]	15.3	13.4	162.3	168.5	0.0908
			1C		
exp.	13.5	13.1	155.4	159.4	0.0847
DFT	13.7	12.5	141.3	150.7	0.0909
DFT in [1Si]	12.4	10.9	146.4	160.5	0.0772

crystal structures. If the lattice parameters are optimized, a higher shrinkage of the unit cell of **1Si** leads to a slightly higher E_{latt}/HS ratio. On the other hand, if the molecule is optimized using the packing pattern of its heteroanalogue, this ratio in both cases is lower by magnitude, which also indicates less favorable packing. Another interesting observation is that both optimized **1C** and **1Si**[1C] structures share virtually the same E_{latt}/HS ratio that is also an indicator of possible polymorphic form for the Si derivative.

In summary, 2,2-dimethoxypropane and dimethyldimethoxysilane were *in situ* crystallized and their previously unknown crystal structures were determined by single-crystal X-ray diffraction analysis. Despite their crystals are not isostructural, they are similar in types and energies of intermolecular interactions, as found by the Hirshfeld surface analysis and a comparison of lattice energies. Based on qualitative differences in crystal packing, the existence of a different polymorphic form of **1Si** isomorphic to **1C** is possible.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.09.018.

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