Thermal properties of \( \text{Zn}_2(\text{C}_8\text{H}_4\text{O}_4)_2 \cdot \text{C}_6\text{H}_{12}\text{N}_2 \) metal-organic framework compound and mirror symmetry violation of dabco molecules

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Thermal properties of \( \text{Zn}_2(\text{C}_8\text{H}_4\text{O}_4)_2 \cdot \text{C}_6\text{H}_{12}\text{N}_2 \) metal-organic framework compound at 8–300 K suggest the possibility of subbarrier tunnelling transitions between left-twisted (S) and right-twisted (R) forms of \( \text{C}_6\text{H}_{12}\text{N}_2 \) dabco molecules with \( \text{D}_3 \) point symmetry. The data agree with those obtained for the temperature behavior of nuclear spin-lattice relaxation times. It is shown that there is a temperature range where the transitions are stopped. Therefore, \( \text{Zn}_2(\text{C}_8\text{H}_4\text{O}_4)_2 \cdot \text{C}_6\text{H}_{12}\text{N}_2 \) and related compounds are interesting objects to study the effect of spontaneous mirror-symmetry breaking and stabilization of chiral isomeric molecules in solids at low temperatures.

Chirality-related interactions are demonstrated by chiral molecules, i.e. those that can exist in both left- and right-handed forms. According to molecular quantum mechanics, such molecules appear in their ground state which is a symmetrical superposition of these two chiral states. However, biological systems are asymmetric (superselection phenomenon) due to fundamental parity violations or the concept of environmental decoherence. As it was discussed earlier, it would be of interest to study the stabilization of chiral molecules in solids at low temperatures to simulate the conditions of the cold scenario. However, the expected fundamental conclusions are still not supported by detailed analysis of the interactions within crystal structures where the stabilization effect is not suppressed by other impacts. In this respect, of high interest are metal-organic framework compounds with large pores, open internal channels, and large internal surface areas.

One such typical example is \( \text{Zn}_2(\text{C}_8\text{H}_4\text{O}_4)_2 \cdot \text{C}_6\text{H}_{12}\text{N}_2 \) crystal. It is composed of tetragonal layers of zinc terephthalic acid \( \text{Zn}(\text{C}_8\text{H}_4\text{O}_4) \) linked by 1,4-diazabicyclo[2.2.2] octane molecules (\( \text{C}_6\text{H}_{12}\text{N}_2 \) or dabco). Dabco molecules have three isomeric forms: one untwisted form with \( \text{D}_3\text{h} \) symmetry, one left-twisted (S) and one right-twisted (R) form with \( \text{D}_3 \) symmetry each (Fig. 1). Dabco molecules are dynamically disordered around the \( \text{c} \) axis of \( \text{Zn}_2(\text{C}_8\text{H}_4\text{O}_4)_2 \cdot \text{C}_6\text{H}_{12}\text{N}_2 \) crystal. The distance between them is ~ 7 Å, so they have no direct contacts with each other.

According to our calculations of isolated dabco molecules, their degenerate energy states correspond to twisted \( \text{D}_3\text{h} \) and \( \text{D}_3 \) forms, and the energy barrier \( (E_b) \) between these two states can vary between 0 and 0.36 kJ/mol depending on the external conditions. Consequently, \( \text{D}_3\text{h} \leftrightarrow \text{D}_3 \) transforms can happen as: (1) barrier-free transitions; (2) activation transitions to overcome the barrier; (3) subbarrier tunnelling transitions. Low activation barrier \( E_a \) between \( \text{D}_3\text{h} \) and \( \text{D}_3 \) forms makes prospective studying tunnelling transitions between these forms, in contrast to those between \( \text{L} \)- and \( \text{D} \)-forms of amino acids in solids with \( E_a \sim 300 \text{ kJ/mol} \) barrier.

The untwisted \( \text{D}_3\text{h} \) state of the dabco molecule corresponds to its transition state and therefore its energy is equal to the value of the energy barrier \( E_b \) (Fig. 1). However, this state can be stable in crystals, and the untwisted molecule can move using both the activation and the tunnelling mechanisms.

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As it was discovered earlier, there are three phase transitions in $\text{Zn}_2(\text{C}_8\text{H}_4\text{O}_4)_2 \cdot \text{C}_6\text{H}_{12}\text{N}_2$14–16. Temperature behavior of spin-lattice relaxation times studied with $^1\text{H}$ NMR $T_1$ demonstrates the effects of tunnelling transitions starting between $D_3(\text{S})$ and $D_3(\text{R})$ forms of dabco molecules at ~165 K, the violation of these transitions at ~60 K, and substantial difference between the values of spin-lattice relaxation data for dabco conformers at < 25 K. In this work we analyze thermal energies of dabco molecules in $\text{Zn}_2(\text{C}_8\text{H}_4\text{O}_4)_2 \cdot \text{C}_6\text{H}_{12}\text{N}_2$ to show that these effects are thermally possible.

Theoretical background
Over-barrier transitions (activation) are characterized by the correlation time

$$\tau_a = \tau_{0a} \cdot \exp \left\{ \frac{E_a}{k_B \cdot T} \right\},$$

where $k_B$ is the Boltzmann constant, $\tau_{0a}$ is the pre-exponential factor for the Arrhenius law, $T$ is the temperature.

Subbarrier tunnelling is described by the Shrödinger equation and is characterized by the correlation time

$$\tau_t = \tau_{0t} \cdot \exp \left\{ \frac{2L}{\hbar} \cdot \frac{2m(E_a - E)}{} \right\},$$

where $m$ is the mass of the tunnelling particle, $\tau_{0t}$ is the pre-exponential factor for tunnelling transitions (inverse vibrational frequency of the particle in the potential well), $E$ is the kinetic (thermal) energy of the particle, $L$ is the width of the activation barrier, $\hbar$ is the Planck constant.

As is well known, thermal energy of atoms and molecules is determined by the temperature of the solid and can be calculated as $E = C_p \cdot T$, where $C_p$ is the thermal capacity of the solid at constant pressure.

In solids, thermal energy is unevenly distributed between atoms and molecules, and at each moment the amplitude and the energy of thermal vibrations for some part of particles can be higher or lower than their average values. To make the transitions possible, some thermal energy is needed. Activation transitions require that some part of particles have $E > E_a$, while tunnelling transitions proceed at $E < E_a$.

We assume that tunneling and activation transitions have the same reaction coordinate. Then for tunnelling transitions with reaction coordinate coinciding with that of reorientational motion (maintaining $D_{3h}$ and $D_{3h}$ symmetries), the minimum distances between the atoms are $D_H = 1.08$ Å (for hydrogen atoms) and $D_C = 0.65$ Å (for carbon atoms). For tunnelling transitions between $D_3(\text{S})$ and $D_3(\text{R})$ these distances are $D_H = 0.66$ Å and $D_C = 0.15$ Å13. Both $D_C$ values are smaller than the covalent radius of the carbon atom ($r_C \sim 0.70$ Å). Hence, we can assume that carbon atoms change their positions during tunnelling without having to overcome a barrier. $D_H$ values exceed the covalent radius of the hydrogen atom ($r_H \sim 0.30$ Å). In this case, the barrier has finite width $L$ and reaches its minimum of ~0.06 Å for tunnelling transitions between $D_3(\text{S})$ and $D_3(\text{R})$ dabco forms. The

![Figure 1. Crystal structure of $\text{Zn}_2(\text{C}_8\text{H}_4\text{O}_4)_2 \cdot \text{C}_6\text{H}_{12}\text{N}_2$, space group $P4/mmm$; $a = 10.93$, $c = 9.61$ Å; $Z = 1$; $T = 223$ K11. Pillar dabco molecules are shown as dynamically disordered (top). Left- and right-twisted $D_3$ and untwisted $D_{3h}$ conformations of dabco molecules (bottom).](image-url)
The double-exponential recovery of FID may indicate that activation mobility of dabco molecules is hindered and all particles to overcome the barrier with energy states were equally stabilized for each conformer. Since $D_3(S)$ and $D_3(R)$ forms are characterized by the same time $T_1$ longer than $T_1L$ and shorter time $T_1S$, above $T_c$ all dabco conformers can overcome barriers $E_a = 0.43$ kJ/gr at and $E_a = 0.22$ kJ/gr at through the activation mechanism, which agrees with $T_1S$ NMR data (Fig. 2). The temperature dependence of $^{1}H$ NMR $T_1$ in $\text{Zn}_2(C_8\text{H}_4\text{O}_4)\cdot\text{C}_6\text{H}_12\text{N}_2$ at 310–165 K obeys the classical theory of nuclear spin-lattice relaxation and is characterized by a single-exponential recovery of the free induction decay (FID).$E_a$ values for dabco molecules. Values $E_a = 0.43$ kJ/gr at corresponds to the calculated $E_a = 7.7$ kJ/mol, respectively. $E_a$ values are assumed to correspond to activation energies only of hydrogen and carbon atoms of the dabco molecule, and nitrogen atoms are not involved in the reorientation. All values of $C_p \cdot T$ and $E_a$ were normalized to one gram-atom to make easier comparison of the results obtained from different methods.

Results and Discussion

Figure 2 presents temperature dependence $C_p \cdot T$, where $C_p$ is the thermal capacity of $\text{Zn}_2(C_8\text{H}_4\text{O}_4)\cdot\text{C}_6\text{H}_12\text{N}_2$ obtained in ref. 17. The same figure shows $E_a$ values for dabco molecules. Values $E_a = 0.22$ kJ/gr at and $E_a = 0.37$ kJ/gr at correspond to experimental values $E_a = 4.0$ kJ/mol and $E_a = 6.6$ kJ/mol, and $E_a = 0.43$ kJ/gr at corresponds to the calculated $E_a = 7.7$ kJ/mol, respectively. $E_a$ values are assumed to correspond to activation energies only of hydrogen and carbon atoms of the dabco molecule, and nitrogen atoms are not involved in the reorientation. All values of $C_p \cdot T$ and $E_a$ were normalized to one gram-atom to make easier comparison of the results obtained from different methods.

Since in Phase I thermal energy $C_p \cdot T > 0.43 > 0.22$ kJ/gr at, above $T_c$ all dabco conformers can overcome barriers $E_a = 0.43$ kJ/gr at and $E_a = 0.22$ kJ/gr at through the activation mechanism, which agrees with $T_1S$ NMR data (Fig. 2). The temperature dependence of $^{1}H$ NMR $T_1$ in $\text{Zn}_2(C_8\text{H}_4\text{O}_4)\cdot\text{C}_6\text{H}_12\text{N}_2$ at 310–165 K obeys the classical theory of nuclear spin-lattice relaxation and is characterized by a single-exponential recovery of the free induction decay (FID).$E_a$ values are assumed to correspond to activation energies only of hydrogen and carbon atoms of the dabco molecule, and nitrogen atoms are not involved in the reorientation. All values of $C_p \cdot T$ and $E_a$ were normalized to one gram-atom to make easier comparison of the results obtained from different methods.

Thermal energy $C_p \cdot T$ in Phase I from 1.0 to 0.2 kJ/gr at. These thermal energies make it impossible for all particles to overcome the barrier with $E_a = 0.43$ kJ/gr at by the activation mechanism, as well as the barrier $E_a = 0.37$ kJ/gr at. Hence, this phase suggests tunnelling transitions. Indeed, at 165–60 K the activation mobility of particles is violated. Firstly, the double-exponential recovery of FID is observed.$E_a$ values for dabco molecules. Values $E_a = 0.43$ kJ/gr at corresponds to the calculated $E_a = 7.7$ kJ/mol, respectively. $E_a$ values are assumed to correspond to activation energies only of hydrogen and carbon atoms of the dabco molecule, and nitrogen atoms are not involved in the reorientation. All values of $C_p \cdot T$ and $E_a$ were normalized to one gram-atom to make easier comparison of the results obtained from different methods.

Thermal energy $C_p \cdot T$ varies in Phase II from 1.0 to 0.2 kJ/gr at. These thermal energies make it impossible for all particles to overcome the barrier with $E_a = 0.43$ kJ/gr at by the activation mechanism, as well as the barrier $E_a = 0.37$ kJ/gr at. Hence, this phase suggests tunnelling transitions. Indeed, at 165–60 K the activation mobility of particles is violated. Firstly, the double-exponential recovery of FID is observed.$E_a$ values for dabco molecules. Values $E_a = 0.43$ kJ/gr at corresponds to the calculated $E_a = 7.7$ kJ/mol, respectively. $E_a$ values are assumed to correspond to activation energies only of hydrogen and carbon atoms of the dabco molecule, and nitrogen atoms are not involved in the reorientation. All values of $C_p \cdot T$ and $E_a$ were normalized to one gram-atom to make easier comparison of the results obtained from different methods.
are small, and reorientation of C8H4O4
tions of intramolecular dipole-dipole interactions, the fluctuations of intermolecular dipole-dipole interactions
which suggests tunnelling of less stable right-enantiomers into more stable left-enantiomers (Salam model)2, 3, 20.

In Phase IV, thermal energy is Cp,T ≤ 0.02 kJ/gr.at. In this case, only tunnelling transitions are possible, and, according to equation (2), time τ1 must reach its highest value here. However, the behavior of τ1 (Fig. 2) does not correspond to classical views on tunnelling processes7, 21, 22. T1 grows when the temperature decreases (like T1 during activation transitions). But there is no consistent activation mobility of the particles neither. Experimental data on time dependences of FID for these temperatures makes it possible to distinguish at least three components (c1, c2, c3) characterized by three different T1 values (Fig. 2). This can mean that D3(S) and D3(R) energies are not equal at the lowest temperatures and that the system as a whole must be characterized by chiral polarization4–16. The discovered difference between T1 times can be considered as an analogue of the previously discovered effect when the multiplicity of the NMR spectrum is doubled when passing from a optically inactive (racemic) to optically active mixtures of chiral isomers35, 36.

As was shown earlier, the mechanism of phase transition from Phase III to Phase IV in our model can be associated with the ordered packing of untunnelling and non-reorienting D3(S) and D3(R) dabco molecules14–16. In this case, violation of D3(S) → D3(R) symmetry can be due to random factors similar to those affecting the precipitation of R- and S-forms of optically active crystals from racemates35. However, the fact that there are three values c1, c2, and c3 (Fig. 2) obtained from the analysis of FID suggests some ambiguity of the proposed model. We can assume that further temperature decrease should lead to further phase transitions and molecular ordering. Also, some additional mechanism to cause non-exponential FID and nuclear spin-lattice relaxations is also possible16.

Note that we do not consider here the mobility of C6H12N2 ⇔ anions, because their high activation barrier (>36 kJ/mol) makes them perform only slow reorientations about the second-order axis. There are no fluctuations of intramolecular dipole-dipole interactions, the fluctuations of intermolecular dipole-dipole interactions are small, and reorientation of C6H12N2 ⇔ anions is not evidenced by 1H NMR T1 measurements14, 26–28.

Conclusions

Thermal properties of Zn2(C6H12O4)•C6H12N2 crystals suggest that there is a possibility that mirror symmetry can be violated between D3(S) and D3(R) forms of dabco molecules. Most interesting are the lowest temperatures where all conformers can be stabilized in their local positions.

Structural transformations associated with the ordering of dynamically disordered dabco molecules in Zn2(C6H12O4)•C6H12N2 during phase transitions can, in principle, be characterized using the approaches described in refs 29 and 30. Here we can only describe the structures expected in different phases. In the high-temperature Phase I, twisted and untwisted dabco molecules are fully disordered. In the Phase II, the crystal structure is built of the chains of dabco molecules, some of which are composed only of untwisted forms and other only of twisted forms. In Phase III, the twisting of dabco enantiomers is expected to be hindered. Finally, when the interaction between the chains becomes prevailing, the crystal structure is supposed to be chirally ordered in Phase IV.

Note that according to a recent study of [Zn2(C6H12O4)•C6H12N2] properties, the Phase II → Phase I transition can be interpreted as an order-disorder phase transition associated with some structural disorder of C6H12O42− anions18. However, dabco molecules remain dynamically disordered and their role in the phase transition is not defined.

Thus, in our opinion, metal-organic framework compound [Zn2(C6H12O4)•C6H12N2] and related crystals10–12, 31 containing racemic mixtures of chiral molecules are convenient systems to develop the approaches aimed at controlling molecular transitions from racemic to chirally polarized states. A special feature of these systems is the absence of direct contacts between chiral molecules in crystals. Such systems are interesting in terms of studying the stabilization of chiral molecules in solids at low temperatures and can serve as models for the conditions of the cold scenario of life origin on the Earth4.

Methods

Heat capacity was measured at 8.98–299.57 K using a computerized vacuum adiabatic calorimeter well tested by measurements of various compounds including sorbents metal-organic framework compound [Zn2(C6H12O4)•C6H12N2]. The details of the synthesis, experimental conditions, and heat capacity values can be found in work37. The 1H NMR spin-lattice relaxation time T1 of [Zn2(C6H12O4)•C6H12N2] was measured with a Bruker SXP 4-100 device at 8–300 K and was previously analyzed in a number of works14–16.

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Author Contributions
Svetlana G. Kozlova did an analysis of the data on the specific heat and a comparison with the NMR data. Syvatoslav P. Gabuda explained the NMR data and proposed a model of the mirror symmetry violation of dabco molecules in the metal-organic framework compound.

Additional Information
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