Introduction

Ethane belongs to the simplest alkanes, present as building blocks in many organic molecules. Therefore, ethane and its derivatives are valuable model compounds for studying molecular aggregation and conformations. The application of halogenated alkanes for improving the technological properties of fuels used for airplanes and improving their security requires information about the structure, aggregation, interactions and thermodynamic properties of these compounds.\(^1\) Halo-substituted methanes exhibit a variety of aggregation modes involving CH⋯halogen and halogen⋯halogen interactions.\(^2\) Haloethanes additionally can change their conformation due to the relatively soft rotations about the C–C bond. Furthermore, the molecules can be orientationally and conformationally disordered.\(^3\) Consequently, haloethanes exist in polymorphic forms and undergo phase transitions involving order–disorder, conformational conversions and changing types of intermolecular interactions.\(^3b,4\) Presently, we have studied the aggregation of pentachloroethane, C\(_2\)HCl\(_5\) (PCE). Its staggered conformation is strongly favored, and the Cl⋯Cl contacts are most likely to dominate its intermolecular interactions. We were particularly interested in the role of CH⋯Cl contacts, which are considerably shorter than halogen bonds Cl⋯Cl and for this reason could be excluded from the main cohesion forces.\(^5\) We have applied high pressure for these studies, because it is the most efficient method for modifying the molecular structure and arrangement in crystals. Therefore, high pressure is increasingly often used for generating new polymorphs of pharmaceutical, energetic and other materials.\(^6\)

Results and discussion

When isothermally compressed in a diamond-anvil cell (DAC), the liquid PCE sample first freezes in orthorhombic phase I and then transforms into monoclinic phase II (see Fig. 1 and Movie S1, ESI†). We determined its structure at 295 K/0.36 GPa and 295 K/0.45 GPa (Table 1). Still higher pressure of ca. 295 K/0.62 GPa induces a reversible discontinuous transition to monoclinic phase II (PCE-II, Fig. 2 and S1, ESI†). We determined the high-pressure structures of PCE-II,
Table 1  Selected crystal data of PCE phases I and II at 295 K. Note the exchanged axes [x] and [y] between phases I and II

|          | PCE-I          | PCE-II         |
|----------|----------------|----------------|
| Pressure, GPa | 0.36(2)        | 0.45(2)        |
| Crystal system | Pnma           | Pnma           |
| a, Å    | 10.325(8)      | 10.210(7)      |
| b, Å    | 11.063(3)      | 11.039(3)      |
| c, Å    | 6.0870(10)     | 6.0415(9)      |
| β, °    | 90             | 90             |
| V, Å³   | 959.3(6)       | 958.9(5)       |

The transition reduces the symmetry of space-group relations indicate that phases I and II are structurally related. The transition reduces the symmetry of space-group Pnma by eliminating the mirror plane and glide plane a. In order to comply with the convention, axes [x] and [y] of phase II have been exchanged and angle β becomes monoclinic in space group P12₁/n (Table 1). The lattice relation between phases I and II implies that parameter a₁ corresponds to b₄ and b₁ corresponds to a₄ (Fig. 4, the subscripts indicate the phases). It also shows that the transition induces a huge strain between phases I and II: axis [x] of phase I expands by over 10%, axis [y] shrinks by nearly ~15%, axis [z] expands by about 6% and a huge shear strain exceeds 21°. All these changes mutually compensate and the resultant volume drop is relatively small.

In both phases I and II, the PCE molecules retain the staggered conformation. In phase I, the molecules are located on mirror planes. Each molecule is involved in two Cl⋯Cl contacts and two CH⋯Cl bonds; the H⋯Cl distance becomes shorter than the sum of van der Waals radii above 0.45 GPa (ref. 7) (Table 2, Fig. 3a).

The pattern of halogen bonds changes between phases I and II (Fig. 3). In phase I at 295 K/0.45 GPa, the Cl⋯Cl bonds arrange molecules into zigzag chains along axis [y] and the voids also assume a zigzag motif of the same direction and period, but much larger amplitude (Fig. 3a). In phase II, the Cl⋯Cl contacts are more numerous and they form a 3-dimensional pattern (Fig. 3b).

The compression of PCE at room temperature (Fig. 4 and S3, ESI†) changes abruptly its volume by −1.3% when the liquid freezes at 0.22 GPa. This molecular-volume drop by 2.4 Å³ is ca. twice smaller than that in 1112TCE (ca. 3.6 Å³, −2.5%)⁴ and it is the smallest volume change reported for chloroethanes,¹⁶,¹⁸,⁵ which also corresponds to the smallest reduction of averaged intermolecular distances for PCE in the pressure region immediately before and above freezing. Then the compression of phase II, between 0.62 and 1.9 GPa, is on average almost three times smaller than that of phase I between 0.22 and 0.62 GPa. The volume discontinuity is very small, but different compression rates clearly distinguish the regions of phases I and II.

In phases I and II, the intermolecular Cl⋯Cl contacts have been compressed to 3.37 and 3.28 Å, respectively. Contacts H⋯Cl are the strongest compressed contacts in phase I, much stronger than contacts Cl⋯Cl. According to the CH⋯Cl bond compression within phase I, it can be estimated that the H⋯Cl distance is less than 2.8 or even 2.7 Å before the transition to phase II. In phase II, the H⋯Cl distance is longer than 3.0 Å and it increases with pressure (Fig. 5). It may indicate that high pressure reduces the potential energy (E_p) associated with the CH⋯Cl bonds in phase I. In phase II, two H⋯Cl contacts, somewhat longer than those in phase I, become longer as pressure increases. At the same time, the compression of contacts Cl⋯Cl in phase II is weaker than that in phase I. It thus appears that the structural rearrangement between phases I and II reverses the compression rate of contacts Cl⋯Cl and H⋯Cl (Tables 2 and 3; Fig. 5 and S4, ESI†). A relatively long, but commensurate with the sum of the van der Waals radii⁷ H⋯Cl/CH⋯Cl intermolecular hydrogen bond was found only in the structure of PCE-I determined at 295 K/0.45 GPa.

The Hirshfeld two-dimensional fingerprint plots show that the H⋯Cl contacts are the most different feature of PCE-I and II (Fig. S5, ESI†), while in both polymorphs the dominant role is played by Cl⋯Cl contacts (Tables 2 and 3). It is
remarkable that in phase I, the C–H⋯Cl bonds are formed, and the Cl⋯Cl contacts do not strictly conform to neither type I nor type II.8

The Cl⋯Cl contacts in phase II can be classified as halogen bonds of types I (Cl2⋯Cl2V) and II (Cl⋯Cl3I) or somewhat distorted from these types (Table 3). The weaker
The van der Waals radii) are the Cl...Cl contacts in phase II and even the negative compression of H...Cl contacts are consistent with the much weaker volume compression of phase II than that of phase I (cf. Fig. 4 and 5).

The shortest intermolecular contacts in the PCE polymorphs can be represented as the diagram of differences between interatomic distances and the sums of van der Waals radii (Fig. 6). It shows that the shortest contacts (related to the van der Waals radii) are the Cl...Cl halogen bonds and only one CH...Cl contact in phase I can be compressed to the third shortest value (the third order), before the crystal transforms to phase II. In phase II, the role of CH...Cl contacts is considerably reduced to the sixth order. Fig. 6 also illustrates the significantly changing role of contacts CH...Cl within phase I. However, the types of shortest contacts in the crystal remain unchanged within the phases and at the phase transition.

**Table 2** Dimensions (Å, °) of the shortest intermolecular contacts in PCE-I at 295 K/0.36 GPa and 295 K/0.45 GPa

| Temperature, K | Pressure, GPa | Cl1...Cl1 | C1...C1 | C1...C1Cl1 | H1...Cl1n | H1...Cl1n-C1nII | C2...ClII | C2...ClII | C2...ClII | Cl1...Cl1-C1 | C1...ClII | C1...ClII-C1nII | C1-C2...ClII-C1nII |
|---------------|--------------|------------|--------|-------------|-------------|-------------------|----------|----------|----------|---------------|--------|-----------------|-----------------|
| 295(2)        | 0.36(2)      | 3.438(11)  | 3.373(10) | 160(2)      | 162(2)      | 180.00(1)         | 175      | 110(3)   | 78(2)    | 180.00(1)     | 180.00 | 180.00          |

Symmetry codes: (I) -x, 1 - y, -1 - z; (II) 1/2 + x, y, -1/2 - z.

**Table 3** Dimensions (Å, °) of the shortest intermolecular contacts in PCE-II at 295 K/0.76 GPa, 295 K/1.00 GPa, 230 K/0.1 MPa and 85 K/0.1 MPa

| Temperature, K | Pressure, GPa | Cl1...Cl3 | C1...C3 | C1...C3Cl1 | H1...Cl1n | H1...Cl1n-C1nIV | C2...ClII | C2...ClII | C2...ClII | Cl1...Cl1-C1 | C1...ClII | C1...ClII-C1nIV | C1-C2...ClII-C1nIV |
|---------------|--------------|------------|--------|-------------|-------------|------------------|----------|----------|----------|---------------|--------|-----------------|-----------------|
| 295(2)        | 0.76(2)      | 3.415(2)   | 3.369(15) | 174.6(4)    | 175.7(4)    | 161.4(4)         | 121.4(3) | 119.6(2) | 121.82(11) | 121.19(6)     | 169(3) | 169(3)          |

Symmetry codes: (I) 1/2 + x, 1/2 + y, 1/2 - z; (II) -1/2 + x, 1/2 - y, 1/2 + z; (III) -x, -y, -z; (IV) 1/2 - x, 1/2 + y, -1/2 - z; (V) 1 - x, -y, 1 - z.

**Conclusions**

In most haloalkanes investigated so far, high pressure favored the CH...halogen bonds more than the halogen...halogen contacts; however in the high-pressure phase II of C2H5Cl the role of the shortest CH...Cl bonds is gradually diminished. It can be assumed that the mechanism leading to this type of transformations involves the limited access to the CH site. The H-bonds have been secluded by the requirement of close packing of the bulky molecules, pushing the CH...Cl bonded groups apart. This effect illustrates one of

![Fig. 5](https://example.com/image.png)

**Fig. 5** The shortest H...Cl and Cl...Cl intermolecular distances (Å) in phases I and II of PCE.
possible mechanisms leading to structural transformations, and in an analogous way to the structures with potential OH⋯O bond donors and acceptors, but without the OH⋯O bonds due to steric hindrances.\(^9\) The room-temperature transition at 0.62 GPa in PCE is one of the still rare examples of the structures, where the shortest intermolecular contact in the low-pressure phase (I) is shorter than the shortest contact in the high-pressure phase (II). A similar relation was observed between the shortest OH⋯O bonds in the low- and high-pressure phases of sucrose.\(^10\) Although phases I and II are structurally related, as indicated by the solid–solid transition, unit-cell dimensions, group–subgroup symmetry relation and similar molecular positions, the transformation induces exceptionally strong strain and rearrangement of molecules, which is consistent with the changes in cohesion forces.

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