Energetics of conformational conversion between 1,1,2-trichloroethane polymorphs†

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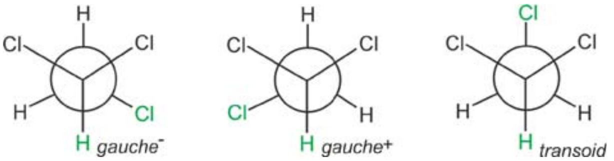
Pressure-induced transformations between *gauche*$^-$, *gauche*$^+$ and *transoid* conformations have been evidenced by X-ray single-crystal diffraction for 1,1,2-trichloroethane, and the energies of intermolecular interactions, conformational conversion, and the latent heat have been determined.

Halogenated ethanes are textbook examples of conformational equilibria and conversions, which are of basic importance for the properties and reactivity of any flexible molecules, and for understanding more complex phenomena, like protein folding and functions of biopolymers.[1] Therefore conformational dynamics and transitions of haloethanes were widely studied by various techniques.[2] It was found that haloethanes form conformational polymorphs, some of them disordered, undergoing solid–solid phase transitions. However, apart from the energy of conformational conversions, the contribution of interactions with molecular environment has not been measured till now. Thus the role of internal and external factors for the molecular conformation is still disputable. The energy of conformers is usually assessed from electrostatic and Lennard-Jones potentials, which are consistent with van der Waals radii and close packing of most molecular crystals.[3] Meanwhile, considerably longer ranges of interactions were recently postulated by Dance[4] and observed in 1,1-dichloroethane.[5]

1,1,2-Trichloroethane, Cl_2CHCH_2Cl (112TCE), is known to exist as *gauche*$^-$ and *gauche*$^+$ conformers, less polar and by 5.9 kJ mol^{-1} more stable[6] than the *transoid* one (Scheme 1).[7] Spectroscopic,[7,8] calorimetric and other studies[6,9] of 112TCE were mainly concerned with its conformers, although no structural data were available. In this study compressibility and low-temperature/high-pressure structural determinations on the single-crystals (Fig. 1) by X-ray diffraction[10]‡ have been employed for documenting the molecular structure and revealing the interplay of interactions and molecular conformations.



Scheme 1 Newman's projections of the 112TCE conformers.

Isobaric freezing of 112TCE at 237 K/0.1 MPa and isochoric freezing at 295 K/0.38 GPa leads to phase α, space group $P12_1/c1$. At 220 K/0.1 MPa the *gauche*$^-$ and *gauche*$^+$ 112TCE molecules are disordered in two orientations at ratio 85 : 15 (and for the sites transformed by inversion centre 15 : 85), respectively. This orientational disorder in phase α exists only close to the freezing curve, and at 100 K/0.1 MPa and at 295 K/0.47 GPa (Fig. 2) the molecules become fully ordered in the dominant conformation. This disorder in 112TCE phase α (Fig. 2 and ESI,† Fig. S2) is analogous to those in other halogenated ethanes, $ClCH_2CH_2Cl$,[2f,11] $Cl_2CHCHCl_2$[12] and ICF_2CF_2I, in this that the Cl/I atoms occupy the common sites and the ethylene moiety is split in two orientations. This type of disorder in 112TCE is optimum for compactly filling the space: the Cl-atoms are located at common sites and disordered H-atoms are very close (Fig. 2). The gradual reduction of the disorder within phase α suggests that it may be dynamical in nature, although such a tumbling requires conformational conversions between *gauche*$^+$ and *gauche*$^-$.

At 295 K/0.82 GPa the 112TCE crystal undergoes a solid–solid transition to phase β, marked by a 5% volume jump (Fig. 3). The space-group symmetry changes from $P12_1/c1$ to $P112_1/n$, molecules move only slightly and the monoclinic direction switches from axis [*y*] to [*z*] (Fig. 2). The discontinuous volume change and no group-subgroup relation between the symmetry classes of phases α and β are characteristic of

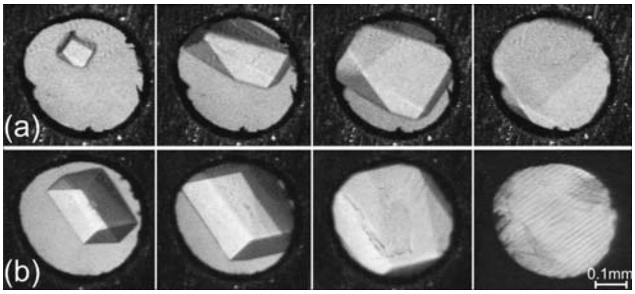


Fig. 1 The 112TCE single-crystal isochoric-growth stages in a diamond-anvil cell. The final pressure for the crystals fully filling the DAC chambers (right photos) are (a) 0.47 and (b) 1.91 GPa.

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† Electronic supplementary information (ESI) available: Details on 112TCE crystallizations, compressibility measurement technique, X-ray diffraction experiments at high pressure and low temperature, solutions and refinements of the crystal structures of 112TCE phases α and β, and molecular geometry calculations. CCDC 680544–680548. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b807372d

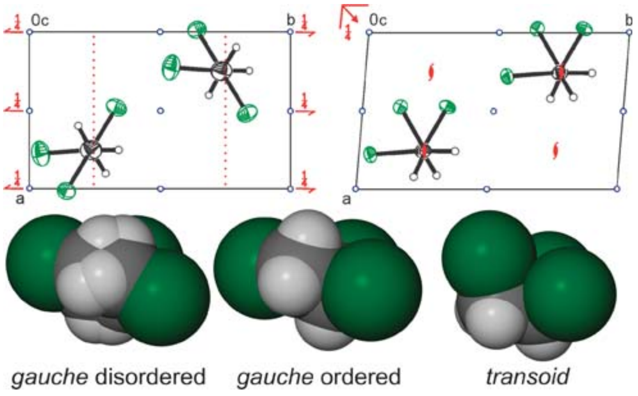

Fig. 2 Corresponding 112TCE molecules related by screw axis 2_1 in phase α (top left, unit-cell outlines and inversion centres are shown in black, and the transforming glide planes and screw axes in red) and glide plane *n* in phase β (top right); and space-filling models of the 112TCE molecules in phase α and β (bottom).

first-order phase transitions. The molecules in phase β assume the *transoid* conformation, and intermolecular H···Cl and Cl···Cl contacts become shorter and some of H···H distances longer than in phase α (Fig. 4, ESI,† Table S2). These structural results are consistent with spectroscopic studies, suggesting that elevated pressure favors the *transoid* conformer in solid and liquid 112TCE and in solutions.[7,8a–c,13]

In phase α, at 220 K/0.1 MPa, there are no contacts shorter than the sums of van der Waals radii,[14] which allows some molecular reorientations. At 100 K/0.1 MPa just one Cl···Cl distance becomes nearly equal to, and at pressure approaching 0.47 GPa shorter than the sum of van der Waals radii (Fig. 4, ESI,† Table S2).

The 112TCE conformation depends on the balance of intramolecular strains and effects of the molecular environment. High-pressure favors the *transoid* conformation that increases the potential energy of molecules, but allows the molecules to pack more efficiently as the accessible volume of molecules is reduced. The volume change ΔV on conversion from *gauche* to *transoid* conformer (in pure 112TCE and in solution) derived from spectroscopic studies[8a–c] ranges from -1.7 to -3.8 cm^3 mol^{-1}. In this study, gas-phase calculations at the HF/6–31+G* and HF/6–311++G** levels[15] yielded the molecular ΔV between -0.6 and -4.4 cm^3 mol^{-1}. The crystal ΔV on entering the β phase of -1.02 cm^3 mol^{-1}, measured directly in the cylinder-and-piston device, substituted to the Clausius–Clapeyron equation gives the transition latent heat of 1.5 kJ mol^{-1} ($\partial p/\partial T$ = 5.1 MPa K^{-1} from ref. 16). This energy compensates the difference between *gauche* → *transoid* conformers and more efficient crystal-packing on transformation from phase α to β, and can be written in the form:

$$E_{\mathrm{inter}}^{\alpha} + E_{\mathrm{conf}}^{\mathrm{gauche}} = E_{\mathrm{inter}}^{\beta} + E_{\mathrm{conf}}^{\mathrm{transoid}} + 1.51\ \mathrm{kJ\ mol^{-1}}$$

where

$$E_{\mathrm{conf}}^{\mathrm{transoid}} - E_{\mathrm{conf}}^{\mathrm{gauche}} = 5.9\ \mathrm{kJ\ mol^{-1}}$$

Thus intermolecular interactions of the rearrangement constitute the main energetic contribution, $E_{\mathrm{inter}}^{\alpha} - E_{\mathrm{inter}}^{\beta} = 7.41$ kJ mol^{-1}, driving this transformation.

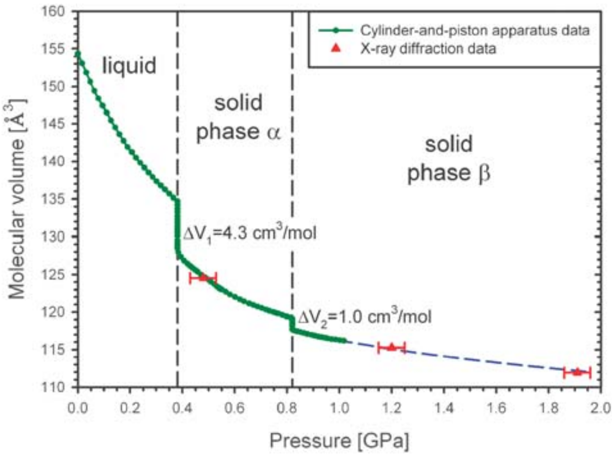

Fig. 3 Molecular volume of 112TCE at 295 K in the function of pressure. The pressure of freezing and of phase α → β transition are marked by volume jumps at 0.38 and 0.82 GPa, respectively.

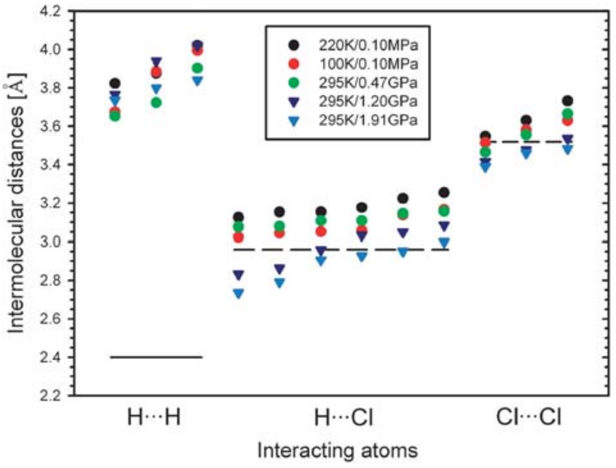

Fig. 4 The evolution of the shortest H···H, H···Cl and Cl···Cl intermolecular distances with temperature and pressure for 112TCE. The horizontal lines mark the sums of van der Waals radii for relevant atoms.

In conclusion, our structural determinations of 112TCE in varied conditions evidenced its conformational conversion, and revealed the energy balance between intra- and intermolecular contributions: 80% of the conversion energy is compensated by the release of lattice-packing interactions, while the latent heat of the transition is a small outcome of the considerable energy transfer in the structure. Analogous energetics can apply also to much more complex systems, *e.g.* to the folding of proteins and reversing handedness of DNA turns,[1] which can be efficiently controlled by external conditions.

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Notes and references

‡ *Crystal data* for 112TCE phase α (CCDC 680544–680546) at: (a) 220 K/0.10 MPa: crystal size 0.30 × 0.20 × 0.20 mm, M_r = 133.39, monoclinic, space group $P12_1/c1$, a = 5.2875(7), b = 8.8172(11), c = 11.1861(12) Å,

β = 93.121(10)°, V = 520.73(11) Å^3, D_c = 1.702 Mg m^{-3}, Z = 4, μ = 1.582 mm^{-1}, reflections collected 3086, R_{int} = 0.0426, data/parameters 939/65, GOF on F^2 1.085, R_1 (all data) = 0.0659, wR_2 (all data) = 0.1386; (b) 100 K/0.10 MPa: crystal size 0.30 × 0.20 × 0.20 mm, M_r = 133.39, monoclinic, space group $P12_1/c1$, a = 5.1516(4), b = 8.5488(6), c = 11.3545(6) Å, β = 92.602(5)°, V = 499.54(6) Å^3, D_c = 1.774 Mg m^{-3}, Z = 4, μ = 1.649 mm^{-1}, reflections collected 3511, R_{int} = 0.0309, data/parameters 904/46, GOF on F^2 1.252, R_1 (all data) = 0.0302, wR_2 (all data) = 0.0554; (c) 295 K/0.47 GPa: crystal size 0.44 × 0.44 × 0.25 mm, M_r = 133.39, monoclinic, space group $P12_1/c1$, a = 5.2539(19), b = 8.698(3), c = 10.948(5) Å, β = 93.01(3)°, V = 499.6(3) Å^3, D_c = 1.773 Mg m^{-3}, Z = 4, μ = 1.648 mm^{-1}, reflections collected 2798, R_{int} = 0.0941, data/parameters 288/46, GOF on F^2 1.179, R_1 (all data) = 0.0572, wR_2 (all data) = 0.1463; and for 112TCE phase β (CCDC 680547 and 680548) at: (a) 295 K/1.20 GPa: crystal size 0.44 × 0.44 × 0.24 mm, M_r = 133.39, monoclinic, space group $P112_1/n$, a = 5.0448(11), b = 8.3551(18), c = 11.006(5) Å, γ = 94.643(18)°, V = 462.4(3) Å^3, D_c = 1.916 Mg m^{-3}, Z = 4, μ = 1.781 mm^{-1}, reflections collected 2125, R_{int} = 0.1048, data/parameters 231/46, GOF on F^2 0.988, R_1 (all data) = 0.0762, wR_2 (all data) = 0.1028; (b) 295 K/1.91 GPa: crystal size 0.44 × 0.44 × 0.23 mm, M_r = 133.39, monoclinic, space group $P112_1/n$, a = 4.9978(15), b = 8.208(3), c = 10.982(4) Å, γ = 94.77(3)°, V = 448.9(3) Å^3, D_c = 1.974 Mg m^{-3}, Z = 4, μ = 1.835 mm^{-1}, reflections collected 2469, R_{int} = 0.2060, data/parameters 353/46, GOF on F^2 1.182, R_1 (all data) = 0.0594, wR_2 (all data) = 0.1151.

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