Conformational conversion in compressed diethyl ether

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Pressure can drastically affect and change the molecular structure and association in the condensed state. Ethoxyethane (diethyl ether, C₄H₁₀O, hereafter ether) is the most common of ethers, known mainly as a solvent generally used in chemical practice and once applied as a general anesthetic. The Raman spectroscopy [1] showed that in the gaseous and liquid states the trans-trans (TT) conformers prevail over trans-gauche (TG) conformers, less stable by ca. 12.6 kJ/mol. For over one hundred years ether is known to occur in two crystal modifications: a stable (m.p. = 157 K) and a metastable (m.p. = 150 K) one.[2] The stable crystal structure of ether (phase α) determined by André et al. (1972) [3] in space group P2₁2₁2₁, Z = 8, comprises two symmetry-independent molecules of the TT conformer. The crystal structure of metastable phase β remains to be determined, but its vibrational spectra indicated, that there are two molecules, both in TT conformation.[4]

In this study we present crystal modifications of ether determined at high pressure. High pressure promotes intermolecular CH∙∙∙O contacts [5,6] and enforces a conversion of its molecular conformation.


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