Photochemistry of bromoform in solution was studied by means of ultrafast time-resolved transient absorption spectroscopy. After 255 nm excitation, bromoform dissociates to the CHBr$_2$ radical and bromine atom, which recombine to form iso-bromoform CHBr$_2$-Br. In nonpolar solvents, such as methylcyclohexane, this isomer has a lifetime significantly greater than time window (1.2 ns), while in polar solvents, such as acetonitrile and methanol, iso-bromoform relaxes to the parent molecule in about 200 ps. This behavior is consistent with DFT intrinsic reaction coordinate calculations of the ground state potential energy surfaces in these solvents. Also, we showed photochemical formation of isomers with Br-Br bond in tribromides of other elements.