Supplementary Information for Conformational studies of 1,2-di-*tert*-butoxyethane with special attention to the *gauche* oxygen effect

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QTAIM analysis

QTAIM analyses and visualization of non-covalent interactions were performed using Avogadro 2.[S1] Quantitative properties including the electron density and its derivatives at bond critical points (BCPs), together with QTAIM atomic charges, were evaluated using critic 2.[S2] The result of QTAIM analysis was shown in Fig. S1.

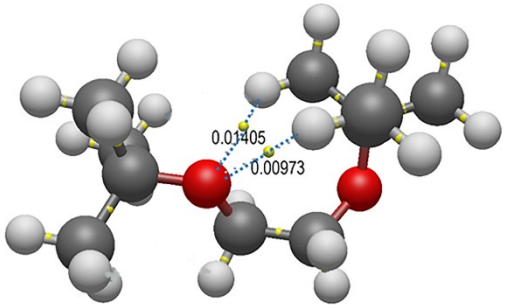

Figure S1. The AIM scheme of the *tgg'* conformer of DTBE in the gas state. Two bond paths indicate the presence of the C-H•••O nonbonding attraction with the electron density at the bond critical points of 0.01405 and 0.00973 a.u. (e a_0^{-3}), respectively.

NBO analysis

Natural bond orbital (NBO) analyses were performed using the NBO 7 module invoked from Gaussian. For each conformer, the optimized geometry was used as input and a single-point calculation was carried out at the same electronic-structure level as adopted in the main text. For calculations in the condensed phase, the polarizable continuum model (PCM) was applied by setting SCRF=(Solvent=acetonitrile). Donor–acceptor interactions were estimated according to the second-order perturbation theory analysis of the Fock matrix, yielding stabilization energies (kcal mol^{-1}) between occupied (donor) and unoccupied (acceptor) NBOs. The discussion focuses on (i) vicinal hyperconjugation of the type σ(C–H)→σ*(C–O), which is commonly invoked to rationalize *gauche* effects, and (ii) n(O) donation into antibonding orbitals, especially LP(O)→σ*(C–H), which may reflect weak C–H···O contacts. The stabilization energies were grouped for the individual conformer (*ttt*, *tgt*, and *tgg'*) and summarized in Table S1.

The NBO analysis of DTBE suggests that the electronic origin of the stabilization of

tgt is more or less similar to those reported for DME by Freitas[S3]: the stabilization due to σ(C–H)→σ* (C–O) interactions integrated per conformer increases from 38.20 (*ttt*) to 50.94 kcal mol^{-1} (*tgt*) in the gas phase, and the difference (*tgt* − *ttt*) amounts to +12.74 kcal mol^{-1}. In the condensed phase such as acetonitrile, the order of free energies is reversed, and *tgt* becomes more stable than *ttt* : ΔG(*tgt*) = −0.58 kcal mol^{-1} (cf. Table 2 and Fig. 6 of the main text). This change is accompanied by a redistribution of the n(O)→σ* contribution, such that the cumulative LP(O)→σ*(C–H) term increases by +5.78 kcal mol^{-1} for *tgt* upon transition from the gas phase to acetonitrile, whereas it decreases by −2.62 kcal mol^{-1} for *ttt* (Table S1). These results suggest that in the transition from the gas phase to polar solvents, in addition to the enhancement of solvation due to the dipole moment, rearrangement of n(O)→σ*-type donor-acceptor interactions may also be involved.

For the *tgg′* conformation, the QTAIM analysis showed the presence of through-space C–H···O contacts (Fig. S1), demonstrating that some close arrangements are indeed possible. Such contacts are expected to appear primarily as LP(O)→σ*(C–H) donations from the NBO perspective, but the corresponding NBO charge-transfer component is small, consistent with a weak interaction. In line with this interpretation, the sum of the stabilization energies for the LP(O)→σ*(C–H) interaction of *tgg′* in the gas phase is 41.34 kcal mol^{-1} (Table S1). Somewhat different from the case of DME, the experimentally high abundance of *tgg′* in the gas phase can be reasonably explained by the cumulative contribution of multiple weak stabilizing interactions, even though gas-phase ΔG calculations based on a single minimum structure place *tgg′* at the higher energy side.

Table S1. Cumulative sum of NBO second-order perturbation stabilization energies (kcal mol^{-1}) for the major donor–acceptor interactions in DTBE in the gas phase and in acetonitrile (MeCN). Each entry represents the sum over all donor–acceptor interactions assigned to the indicated interaction type. Δ_{M-G} denotes MeCN − Gas.

Conformer	σ(C–H)→σ*(C–O)			LP(O)→σ*(C–H)		
□	Gas	MeCN	Δ_{M-G}	Gas	MeCN	Δ_{M-G}
ttt	38.20	39.50	1.30	49.06	46.44	-2.62
tgt	50.94	50.32	-0.62	39.66	45.44	5.78
tgg′	55.86	56.92	1.06	41.34	40.24	-1.10

References

S1. M. D. Hanwell, D. E. Curtis, D. C. Lonie, T. Vandermeersch, E. Zurek, and G. R.

Hutchison, *J. Chem. Inform*. 2012, **4,** 17. https://doi.org/10.1186/1758-2946-4-17

S2. A. Otero-de-la-Roza, E. R. Johnson, V. Luaña, *Comput. Phys. Commun.* 2014, **185**, 1007–1018. https://doi.org/10.1016/j.cpc.2013.10.026

S3. M. P. Freitas, *ChemPhysChem*, 2025, **26**, e202500458.