

**Electronic supplementary information of**  
**“Isomer-selective infrared spectroscopy of the cationic**  
**trimethylamine dimer to reveal its charge sharing and**  
**enhanced acidity of the methyl groups”**

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## Optimized structures of the TMA dimer cation

### S1-1 Optimized structures at the $\omega$ B97X-D/6-311++G(3df, 3dp) level

Fig. S1-1 shows the optimized structures of TMA dimer cation at the  $\omega$ B97X-D/6-311++G(3df,3dp) level. The isomeric structures of Figs. S1-1(a), (b), and (c) are the same as those in Figs. 3(a), (b), and (c) in the main text, respectively.

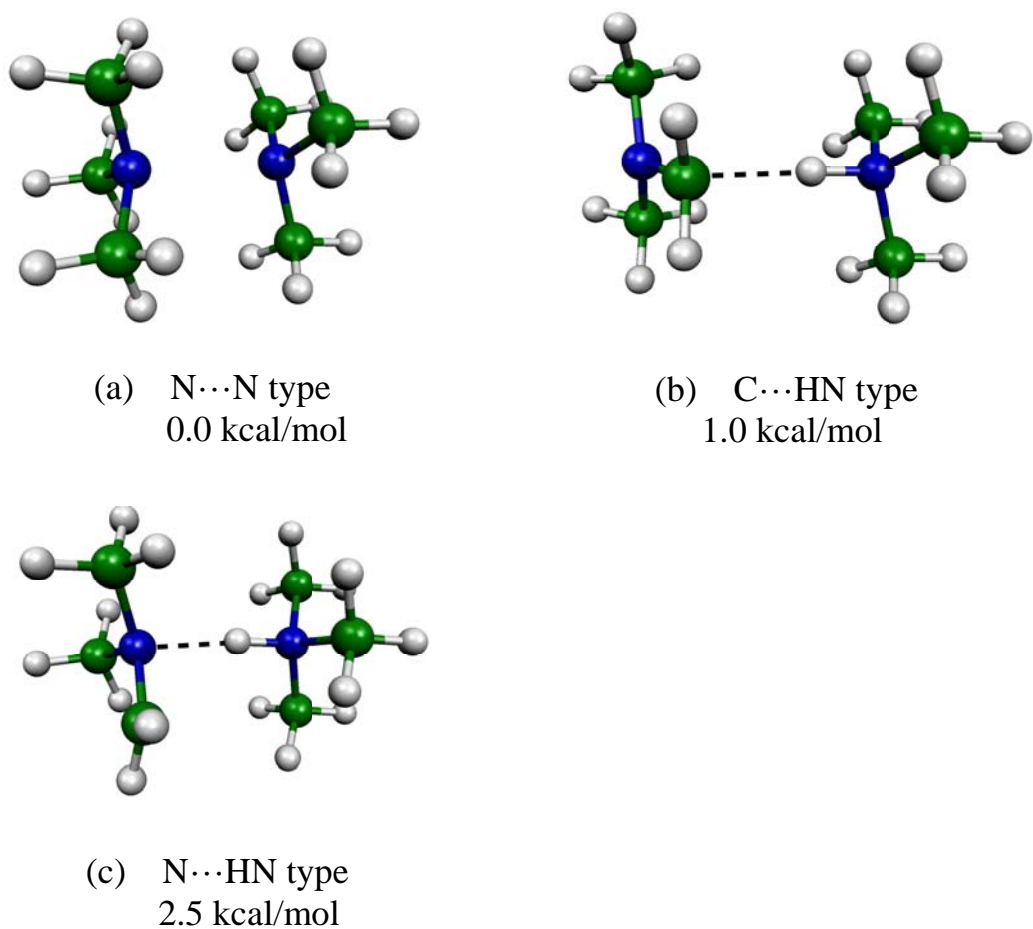


Fig. S1-1 Optimized structures of the TMA dimer cation at the  $\omega$ B97X-D/6-311++G(3df,3dp) level. The relative energies shown in the figure are corrected by the zero-point energies.

### S1-2 Optimized structures at the M06-2X/6-311++G(2d, 2f) level

Fig. S1-2 shows the optimized structures of the TMA dimer cation at the M06-2X/6-311++G(2d,2p) level.

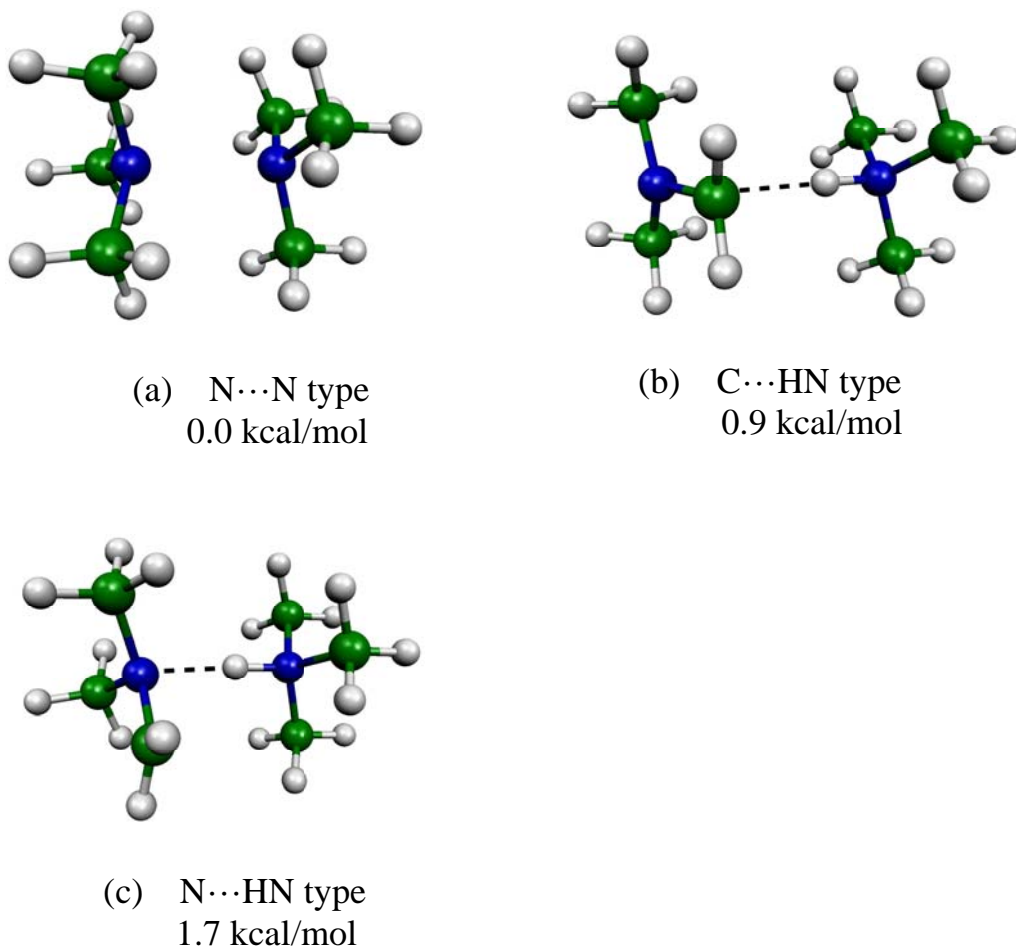


Fig. S1-2. Optimized structures of the TMA dimer cation simulated at the M06-2X/6-311++G(2d,2p) level. The relative energies shown in the figure are corrected by the zero-point energies.

### S1-3 Optimized structures at the PBE1PBE/6-311++G(2d, 2f) level

Fig. S1-3 shows the optimized structures of the TMA dimer cation at the PBE1PBE/6-311++G(2p,2d) level.

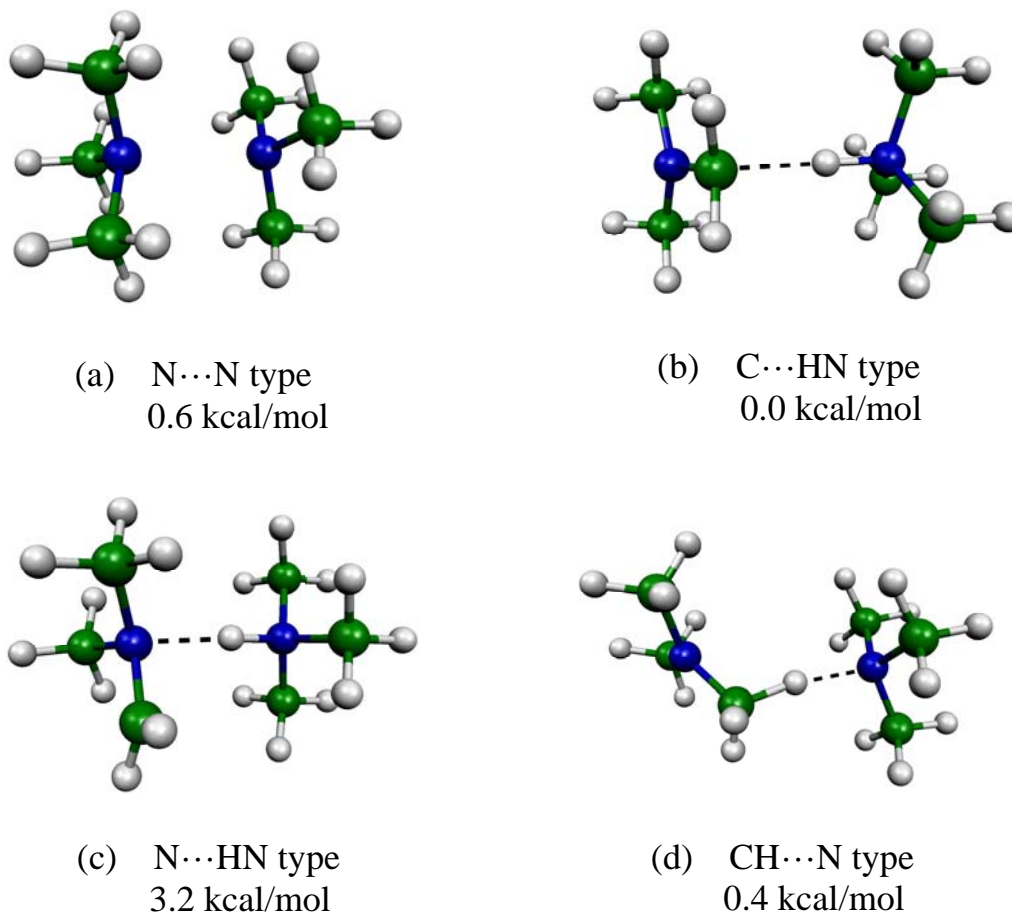


Fig. S1-3 Optimized structures of the TMA dimer cation simulated at the PBE1PBE/6-311++G(2d,2p) level. The relative energies shown in the figure are corrected by the zero-point energies.

At the PBE1PBE level, structure (b) is calculated as the most stable structure and structure (d) is also found as a stable structure. At the PBE1PBE/6-31+G\* level, the

energy barrier between structures (b) and (d) is estimated to be 1.3 kcal/mol by changing the C-H bond distance of the proton donor moiety and optimizing all the other structural parameters. This barrier is lower than the zero-point energies of these isomers. Therefore, the potential energy landscape at the PBE1PBE/6-311++G(2d,2p) level is essentially same as those at the other calculational levels. Although the proton-transfer potential profile might be slightly affected by the calculational methods, this calculational level dependence does not change our conclusion of the high acidity of the cationic CH bond. The observed infrared spectral profile also demonstrates this conclusion, described in the text.