Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Pseudorotaxanes in the Gas Phase: Structure and Energetics of Protonated Dibenzylamine–Crown Ether Complexes

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Electronic Supplementary Information

Table S1. Total energy (kJ mol^{-1}) of stable isomers for the dBAMH$^+$–15C5, dBAMH$^+$–18C6, and dBAMH$^+$–24C8 complexes calculated at the M05-2X/6-3111++G(d,p) level. The energy is corrected with zero-point vibrational energy. The characters in parentheses stand for the conformation of the dBAMH$^+$ part in the complexes (see Figure 3).

	dBAMH$^+$–15C5	dBAMH$^+$–18C6	dBAMH$^+$–24C8
I	0 (C)	0 (B)	0 (A)
II	3.1 (C)	1.3 (C)	0.0 (A)
III	3.8 (C)	2.0 (C)	3.5 (A)
IV	4.1 (C)	3.1 (B)	4.0 (A)
V	4.2 (C)	3.6 (C)	4.5 (A)
VI	4.4 (C)	5.9 (C)	11.3 (A)
VII	9.7 (C)	10.9 (C)	12.5 (A)

Figure S1 shows the ^{1}H NMR spectra of dBAMH$^+$•PF$_6^-$, 15C5, 18C6, 24C8, and their mixtures recorded at 300 MHz in CD$_3$OD at room temperature. For bare dBAMH$^+$, the CH$_2$ protons show a signal at 4.20 ppm (Figure S1a). The 15C5, 18C6, and 24C8 ethers have a strong signal of the oxyethylene protons at ~3.64 ppm (Figures S1b, d, and f). For the mixtures of dBAMH$^+$ with 15C5, 18C6, or 24C8 (Figures S1c, e, and g), only the 24C8 case (Figure S1g) shows signals assignable to the complex. The oxyethylene protons of 24C8 show an up-field shift from 3.64 to 3.48 ppm by the complex formation. The signal of the CH$_2$ protons of dBAMH$^+$ shifts the position from 4.20 to 4.62 ppm. The absence of a complex signal for 15C5 and 18C6 indicates that the equilibrium constant is very small for the dBAMH$^+$•15C5 and dBAMH$^+$•18C6 complexes in solution. In sharp contrast, dBAMH$^+$ can form a stable, long-lived complex with 24C8 in solution at room temperature. From the relative intensity of the NMR signals between bare species and the dBAMH$^+$•24C8 complex in Figure S1g, roughly a half of dBAMH$^+$ in solution forms a complex, probably a pseudorotaxane, just by being mixed with 24C8. The NMR measurements described above suggest that the dBAMH$^+$•15C5 and dBAMH$^+$•18C6 complexes in our gas-phase experiment are produced not in solution but at somewhere between the ESI source and the QIT. It should be noted that the detection of complexes in mass spectra by using ESI sources is not necessarily a direct evidence of the formation of stable complexes in solution.

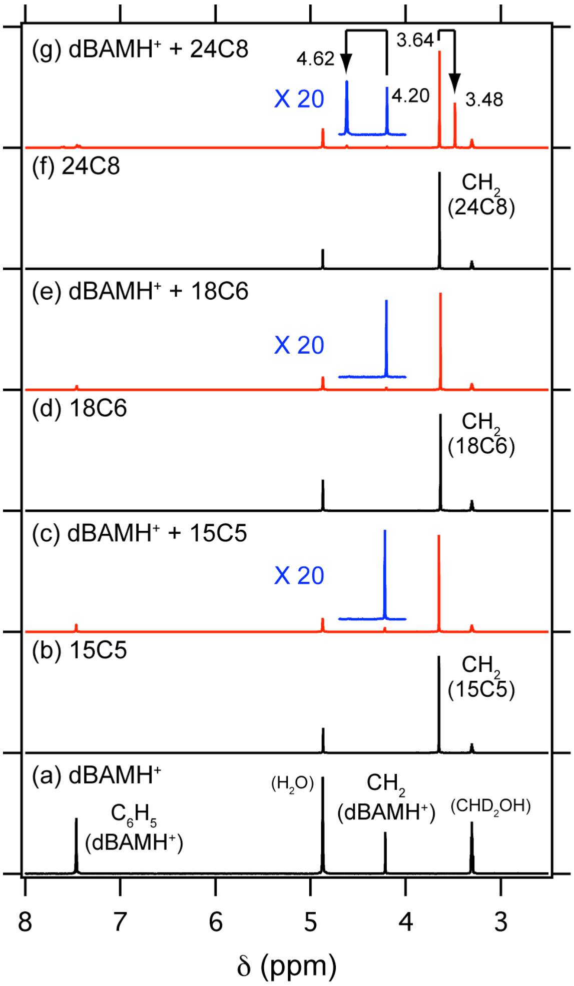

Figure S1. ^{1}H NMR spectra of dBAMH$^+$, 15C5, 18C6, 24C8, and their mixtures recorded at 300 MHz in CD_3OD solution at room temperature.

Table S2. Relative energies (kJ mol^{-1}) of the dBAMH$^+$ conformers with the 6-311++G(d,p) basis set.

isomers	M05-2X	wB97X-D
Isomer A	0	0
Isomer B	0.6	-0.1
Isomer C	3.0	1.0

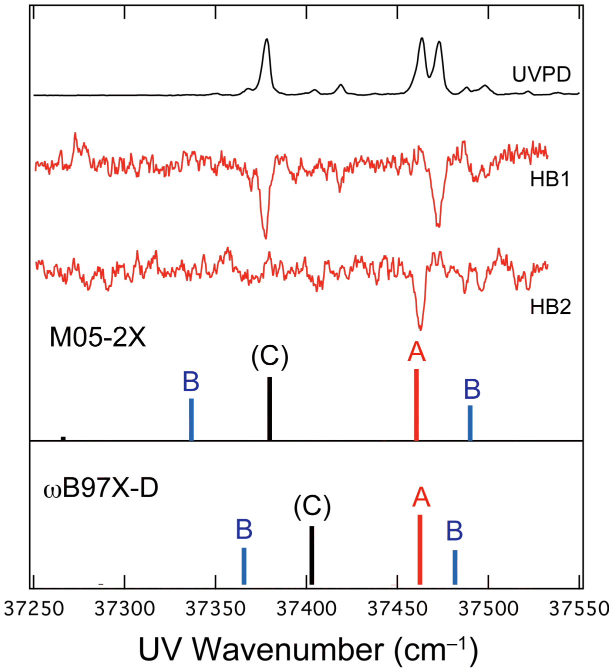

Figure S2. UV spectra of dBAMH$^+$.