

Interaction of Hydronium Ion with Dibenzo-18-crown-6: NMR, IR, and Theoretical Study

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Interaction of dibenzo-18-crown-6 (DBC) with H_3O^+ (HP) in nitrobenzene-*d*₅ and dichloromethane-*d*₂ was studied by using ¹H and ¹³C NMR spectra and relaxations, FTIR spectra, and quantum chemical DFT calculations. NMR shows that the DBC•HP complex is in a dynamic equilibrium with the reactants, the equilibrium constant *K* being 0.66×10^3 , 1.16×10^4 , and $1.03 \times 10^4 \text{ L} \cdot \text{mol}^{-1}$ in CD_2Cl_2 , nitrobenzene, and acetonitrile, respectively. The complex appears to have a C_{2v} symmetry in NMR, but FTIR combined with DFT normal mode calculations suggest that such high symmetry is only apparent and due to exchange averaging of the structure. FTIR spectra as well as energy-optimized DFT calculations show that the most stable state of the complex in solution is that with three linear hydrogen bonds of HP with one $\text{CH}_2\text{—O—CH}_2$ and two Ar—O—Ar oxygen atoms. The structure is similar to that found in solid state but adopts a somewhat different conformation in solution. The dynamics of exchange between bound and free DBC was studied by NMR transverse relaxation. It was found to be too fast to give reproducible results when measured with the ordinary CPMG sequence or its variant DIFTRE removing residual static dipolar interaction, but it could be established by rotating-frame measurements with high intensity of the spin-lock field. The correlation time of exchange was found to be 5.6×10^{-6} and $3.8 \times 10^{-6} \text{ s}$ in dichloromethane and nitrobenzene, respectively. Such fast exchange can be explained by cooperative assistance of present water molecules.

Introduction

Crown ethers have been under scrutiny mainly because of their phenomenal ability to bind various cations.^{1–3} Whereas binding of metal cations has been of interest in analytical or synthetic organic chemistry, the interaction with various forms of hydrated proton (HP) such as hydronium ion H_3O^+ or higher hydrates (H_5O_2^+ and others) stimulate theoretical studies of the relation between the steric properties of the crown cavity and the direction and the strength of the complex-forming hydrogen bonds.^{4–9}

In the case of dibenzo-24-crown-8, the complex with H_5O_2^+ was isolated, and its crystal structure was established by X-ray.⁴ The structure, stability, and exchange dynamics of the same complex in nitrobenzene solution was studied by NMR and quantum chemical DFT calculations.¹⁰ In spite of the high stability of the complex (the equilibrium constant being over $10^6 \text{ L} \cdot \text{mol}^{-1}$), the exchange of H_5O_2^+ between crown molecules is quite swift, with the correlation time τ_{ex} approximately 0.8 ms.

The next symmetric 18-crown-6 with its derivatives is interesting because of its selectivity^{6–9,11–13} of binding the hydronium ion H_3O^+ : the next proton hydrate H_5O_2^+ is too large to fit into the cavity of the polyether ring, and its complex with two crown molecules, as apparently possible with even smaller crown ethers,^{7,14} is much less stable. The apparent simplicity of the asymmetric $\nu(\text{COC})$ stretching band in the infrared spectrum of the H_3O^+ •18-crown-6 complex led to the suggestion⁷ of either bifurcated hydrogen bonds or rapidly rotating

ion in the complex. However, theory predicts⁵ three linear hydrogen bonds as the most stable state, whereas the state with bifurcated hydrogen bonds, actually a transition state of the ion rotation, is predicted to have a higher energy by 4–5 kcal/mol. High-precision DFT calculations confirm⁸ the correspondence of the observed infrared spectrum with theoretical prediction of three symmetric linear hydrogen bonds in the complex. Numerous X-ray studies⁹ of the H_3O^+ •18-crown-6 complex with various anions also suggest such structure although neutron diffraction would be needed for quite precise localization of the hydronium ion protons.

In the complex of hydronium ion with asymmetric benzo-18-crown-6, no indication of ultrafast rotation of the ion or abnormal hydrogen bonds can be detected in infrared spectra.⁷ Although the accumulated results appear to rule out these possibilities even in the case of the symmetric 18-crown-6, there is a very slight possibility that symmetry could play some role in the binding mode. Dibenzo-18-crown-6 (DBC) has a degree of symmetry standing between the just mentioned cases. It is thus interesting to study its interaction with the hydronium ion H_3O^+ . We present the study in solution by using solvents with markedly differing polarity and dielectric properties, namely, nitrobenzene-*d*₅ and acetonitrile-*d*₃ ($\epsilon = 35.6$ and 36.6 , respectively) and dichloromethane-*d*₂ ($\epsilon = 8.93$), so that the influence of the medium's polarity can be observed. As in our previous studies of the interaction of oxonium ions with various ligands,^{15–21} hydrogen bis(1,2-dicarbolyl) cobaltate (HDCC)¹⁵ was used as a reliable source of protons, which were converted to oxonium ions by a 3.5 mol/mol excess of water present in the superacid. From the variety of various proton hydrates present under such conditions, that is, H_3O^+ , H_5O_2^+ , and even H_7O_3^+ , only hydronium ions H_3O^+ are known to fit into the 18-crown-6 cavity. Because the proton exchange between

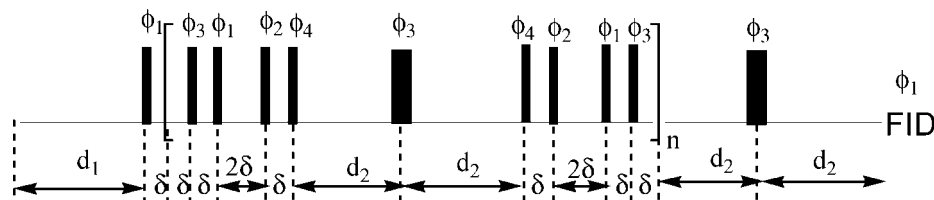
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SCHEME 1: DIFTRE Pulse Sequence



The slim bars mean 90° pulses, the thick ones mean 180° pulses.

various hydrates is very fast, the higher hydration state is no obstacle of the hydronium ion interaction with the crown ether.

Experimental Section

Materials and Samples. DCB was purchased from Fluka and used as obtained. Hydrogen bis(1,2-dicarbolyl) cobaltate (HDCC) was prepared from cesium bis(1,2-dicarbolyl) cobaltate (HDCC) by the method published elsewhere¹⁵ and dried under vacuum for several weeks. In its final state, it still contained 3.5 mol H_2O per 1 mol HDCC. Nitrobenzene- d_5 , acetonitrile- d_3 , and dichloromethane- d_2 were purchased from Sigma-Aldrich and dried over a molecular sieve before use. All samples for NMR measurements contained 0.02 mol/L of DBC and 0.01, 0.02, 0.03, 0.04, or 0.08 mol/L of HDCC in nitrobenzene- d_5 or dichloromethane- d_2 . The samples were stored and measured at 295 K.

NMR Spectra. ^1H and ^{13}C NMR spectra were measured in a quadrature detection mode at 300.13 and 75.45 MHz, respectively, with an upgraded Bruker Avance DPX300 spectrometer. A total of 32 and 64 kpoints were measured for ^1H and ^{13}C NMR, respectively. In order to improve the sensitivity as well as to avoid obscuring strong signals of nitrobenzene, ^{13}C NMR measurements were performed by using ^1H - ^{13}C polarization transfer, namely, combining DEPT sequences²² (by using a $\pi/8$ read pulse and collecting 8000 scans) optimized for J_{CH} 145 and 12 Hz. Exponential weighting ($\text{lb} = 1$ Hz) was used before Fourier transform. In ^1H - ^{13}C 2D HSQC and HMBC spectra used for signal assignment, 1028 points in F2 and 256 increments in F1 dimensions were measured by using a z -gradient inverse-detection probe. For all the following methods inspecting exchange dynamics, the robust proton decoupler channel of a broadband probe was used. The Carr-Purcell-Meiboom-Gill (CPMG) sequence²³⁻²⁵ was used with the delay t_p between π pulses 2.0, 1.0, 0.5, 0.25, and 0.125 ms (the length of the π pulse was 31.2 μs). A total of 32 increments with the total sequence length progressively increased by 40 ms were measured in each experiment, and the measurements were repeated at least three times until their difference was at most 3 relative %. $T_{1\rho}$ measurements^{26,27} were measured with a pulsed spin-lock field ω_1 in the intensity 1.53×10^3 , 3.05×10^3 , 6.1×10^3 , 1.22×10^4 , 2.44×10^4 , and 4.88×10^4 rad/s by using the MLEV17 pulse sequence provided by the Bruker software. A total of 32 increments distanced 20 ms were measured in one experiment. The pulse sequence for static dipolar interactions free transverse relaxation (DIFTRE)¹⁰ combines WHH4²⁸ and CPMG²³ sequences. The pulse sequence is depicted in Scheme 1. The phase cycling was $\phi_1 = x, -x, -x, x, y, -y, y$; $\phi_2 = -x, x, x, -x, -y, y, y, -y$; $\phi_3 = y, -y, -y, y, -x, x, x, -x$; $\phi_4 = -y, y, y, -y, x, -x, -x, x$. The delays d_1 (recovery) and d_2 (transverse relaxation, $t_p/2$) were adjusted in analogy with the above-described CPMG measurements, and δ was optimized to 20 μs for the 15.6 μs $\pi/2$ pulses.

Infrared Spectra. FT IR spectra of the nitrobenzene- d_5 and CD_2Cl_2 solutions were measured at ambient temperature with

a Nicolet Nexus 870 FTIR spectrometer purged with dry air and equipped with a cooled MCT detector. Samples were measured in the NaCl cell (0.036 mm). The spectra were corrected for absorption of the solvent and H_2O vapors.

Quantum Mechanical Calculations. Quantum mechanical calculations were carried out at the density functional level of theory (DFT) by using the Gaussian 03 suite of programs.²⁹ All geometries have been fully optimized without restrictions with the B3LYP functional and the 6-31G(d) basis set. Harmonic vibrational frequencies and infrared band intensities of the normal modes were calculated at the B3LYP/6-31G(d) level, and all reported vibrational frequencies were scaled³⁰ by the standard scaling factor of 0.961.

Results and Discussion

1. Structure of the Complex. 1.1. NMR Spectra. Figure 1 shows 300.13 MHz ^1H NMR spectra of 0.02 mol/L solution of DBC in nitrobenzene- d_5 and its mixtures with gradually increasing amounts of HDCC. Because of practically complete ionization of HDCC in the medium, the concentration of HDCC can be taken as equal to that of protons or rather their hydrated form (HP). The signal assignment in this and all other NMR spectra corresponds to Scheme 2A, where the numbers refer to carbon atoms and protons attached to them.

The shape of the spectrum of DBC itself indicates a high degree of symmetry (C_{2v}), which is consistent with the structure in Scheme 1. As it will be shown below, DBC has a number of mutually similar conformations, mostly symmetric but slightly different, so that the spectrum probably reflects an exchange-averaged structure. Protons 2 and 3 resonate at very similar frequencies so that we have an A_2B_2 multiplet for them.

When the concentration of HP (or HDCC) is increased in the system, all signals of DBC gradually shift without increasing their number. From this, the following conclusions can be drawn: (i) H_3O^+ interacts with DBC forming a complex in solution with a slightly different electron density distribution and/or conformation, compared to free DBC; (ii) the exchange between bound and free DBC must be fast so that we see exchange-averaged signals; (iii) the symmetry of the complex is either similar to that of the free DBC or it is only apparent, the shape of the spectrum being a result of exchange averaging; (iv) from the fact that the DBC signals continue to shift at HDCC/DBC ratios larger than 1.0, one could assume that more than one H_3O^+ ions can combine with the DBC molecule; however, as it will be shown in the next section, this phenomenon is explained better by the equilibrium between free DBC and equimolecular $\text{H}_3\text{O}^+\cdot\text{DBC}$ complex.

The same conclusions (i)–(iii) can be drawn from the shape of ^{13}C NMR spectra shown in Figure 2. Again, the relative signal shifts caused by interaction with H_3O^+ show marked change in electron density distribution in DBC but do not indicate any change in its symmetry.

Considering the most probable structure of the complex shown schematically in Scheme 2B (cf. also the calculated

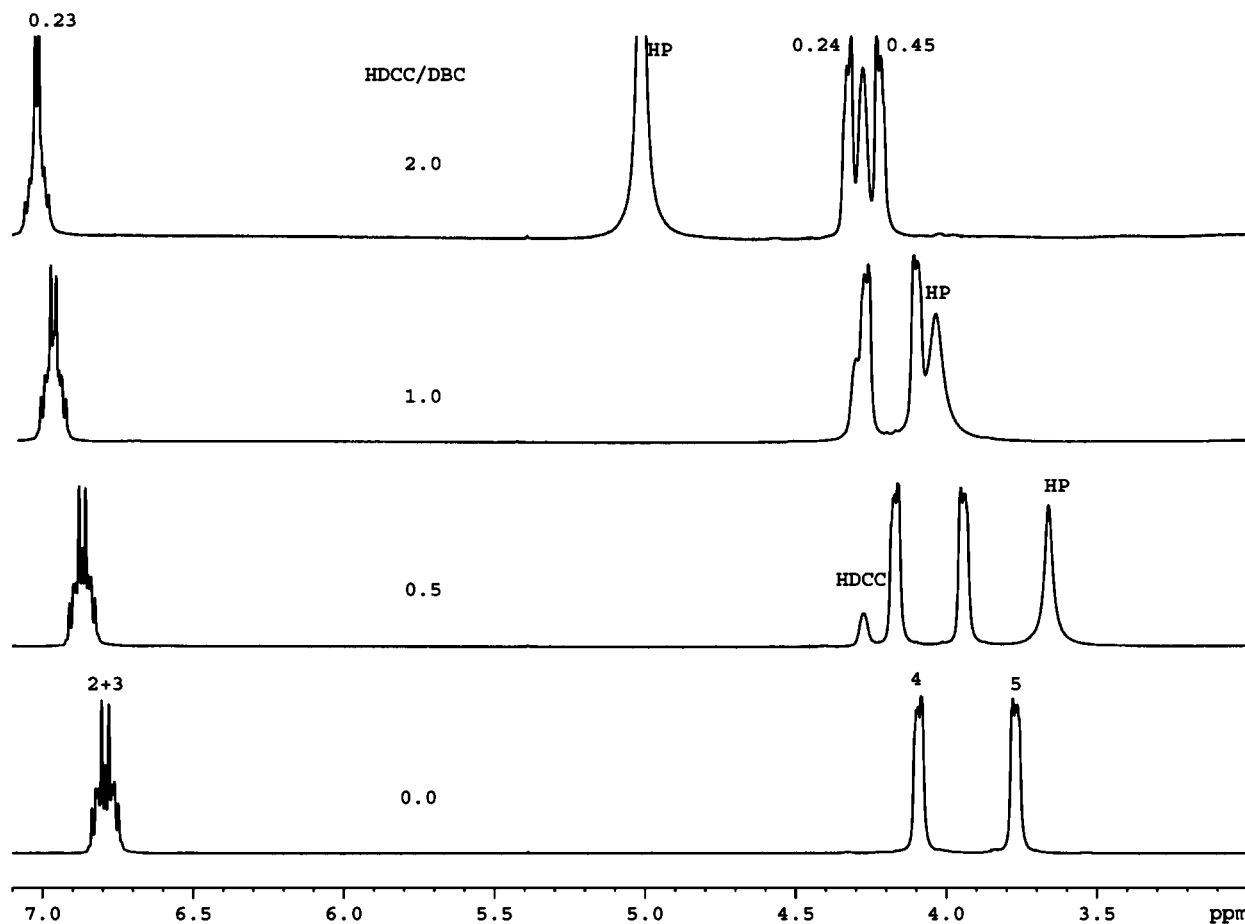
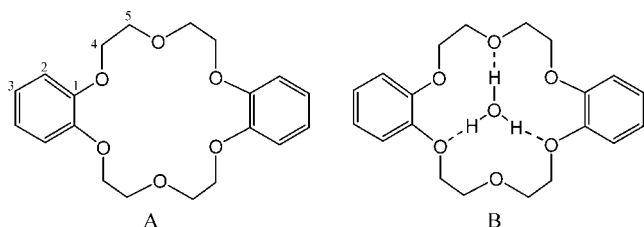


Figure 1. 300.13 MHz ^1H NMR spectra of 0.02 mol/L DBC and its mixtures with HDCC under the indicated HDCC/DBC ratio (nitrobenzene- d_5 , 295 K; HDCC means a signal of one of the protons of the DCC^- anion). Signal assignment is in the bottom spectrum, and maximum relative shift of the signals is in the uppermost one.

SCHEME 2: Numbering of the Carbon (and Attached Proton) Atoms in DBC (A) and the Most Probable Structure of the $\text{H}_3\text{O}^+\cdot\text{DBC}$ Complex (B)



structures below), the retention of the C_{2v} symmetry is not probable. On the other hand, there is a fully equivalent variant of this structure corresponding to the 60° turn of H_3O^+ around the oxygen atom. Therefore, the apparent symmetry is probably due to exchange averaging of the structure, either fast (in NMR time-scale) rotation of H_3O^+ within the complex or intermolecular exchange between bound and free H_3O^+ .

In order to check the possible influence of the polarity of the medium on the above results, we made the same experiments in CD_2Cl_2 with a dielectric constant about four times lower than that of nitrobenzene. Some of the proton spectra are shown in Figure 3. Comparison with Figure 1 shows that the general trends just described are quite analogous, with a few differences: (a) the relative shifts due to binding of H_3O^+ are generally lower here; (b) the equilibrium is less shifted toward the complex (see next section); (c) in particular, the signals of protons 2 and 3 have chemical shifts almost identical in free DBC but markedly

different in the complex, which is quite to the contrary to the situation in nitrobenzene. Whereas (b) can be easily explained by the lower ionization of HDCC in dichloromethane, (a) and in particular (c) must have more complex reasons. Very probably, the most stable conformations both of DBC and its complex are somewhat different in the two media because of their different polarity and perhaps specific interactions in the case of nitrobenzene.

1.2. FT IR Spectra. Figure 4 compares $\nu_{\text{as}}(\text{C}-\text{O}-\text{C})$ regions of FT IR spectra of DBC and its 1:1 and 1:2 mol/mol mixtures with HDCC in CD_2Cl_2 (the IR spectra of the analogous mixtures in nitrobenzene- d_5 are quite similar). As one can see, a new band is formed at 1098 cm^{-1} , which is the most prominent sign of the formed $\text{H}_3\text{O}^+\cdot\text{DBC}$ complex and corresponds to $\text{C}-\text{O}-\text{C}$ stretching coupled with H_3O^+ bending (see below). As a whole, the bands of the spectrum cannot be assigned to individual vibrations because of their interconnection and overlap (besides $\text{C}-\text{O}-\text{C}$ vibrations, there are, for example, aromatic $\text{C}-\text{H}$ in-plane deformation vibrations in the region). A much more realistic approach is the comparison of the vibration modes calculated for a given molecular form with the actual experimental spectrum.

Figure 5 shows the calculated normal vibration modes of the theoretically most stable configuration of $\text{H}_3\text{O}^+\cdot\text{DBC}$ complex (see below) and the simulated IR spectrum. The calculated normal vibration mode at 1082 cm^{-1} in $\text{DBC}-\text{H}_3\text{O}^+$ complex corresponds to the $\text{C}-\text{O}-\text{C}$ stretching strongly coupled with H_3O^+ bending. As one can see by comparison with Figure 4, there is a usual shift both in vibration frequencies and absor-

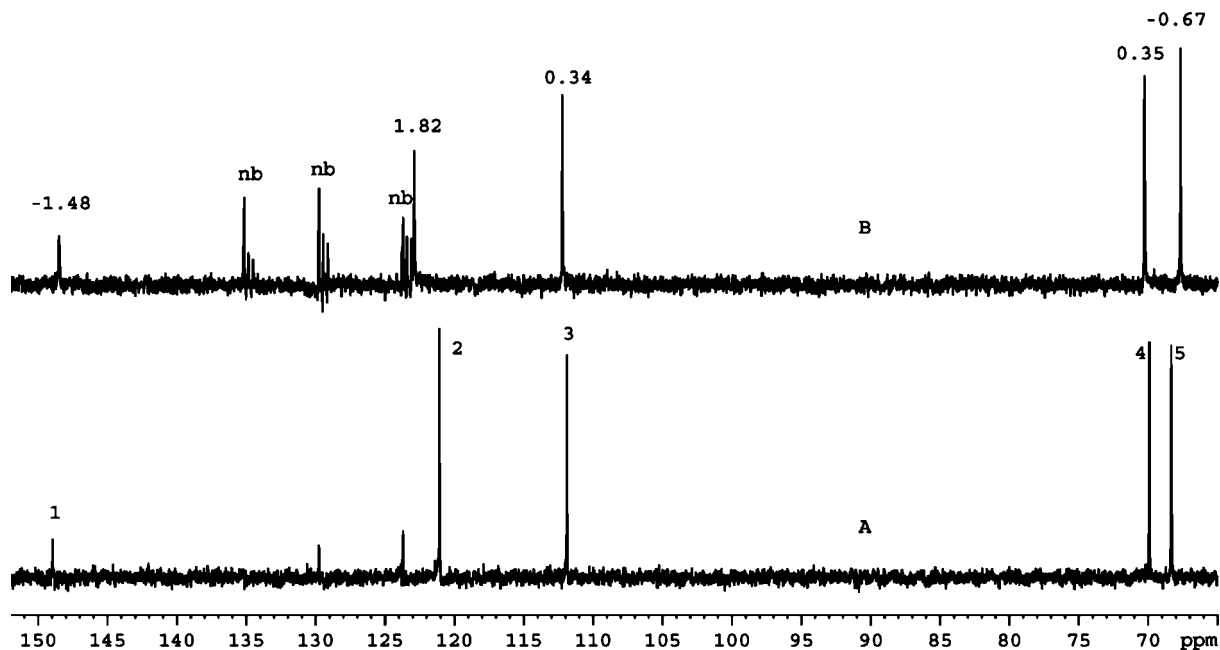


Figure 2. 75.45 MHz ^{13}C NMR spectra of 0.02 mol/L solution of DBC (A) and its 1:2 mol/mol mixture with HDCC (B) (nitrobenzene- d_5 , 295 K). Maximum shifts are given in panel B.

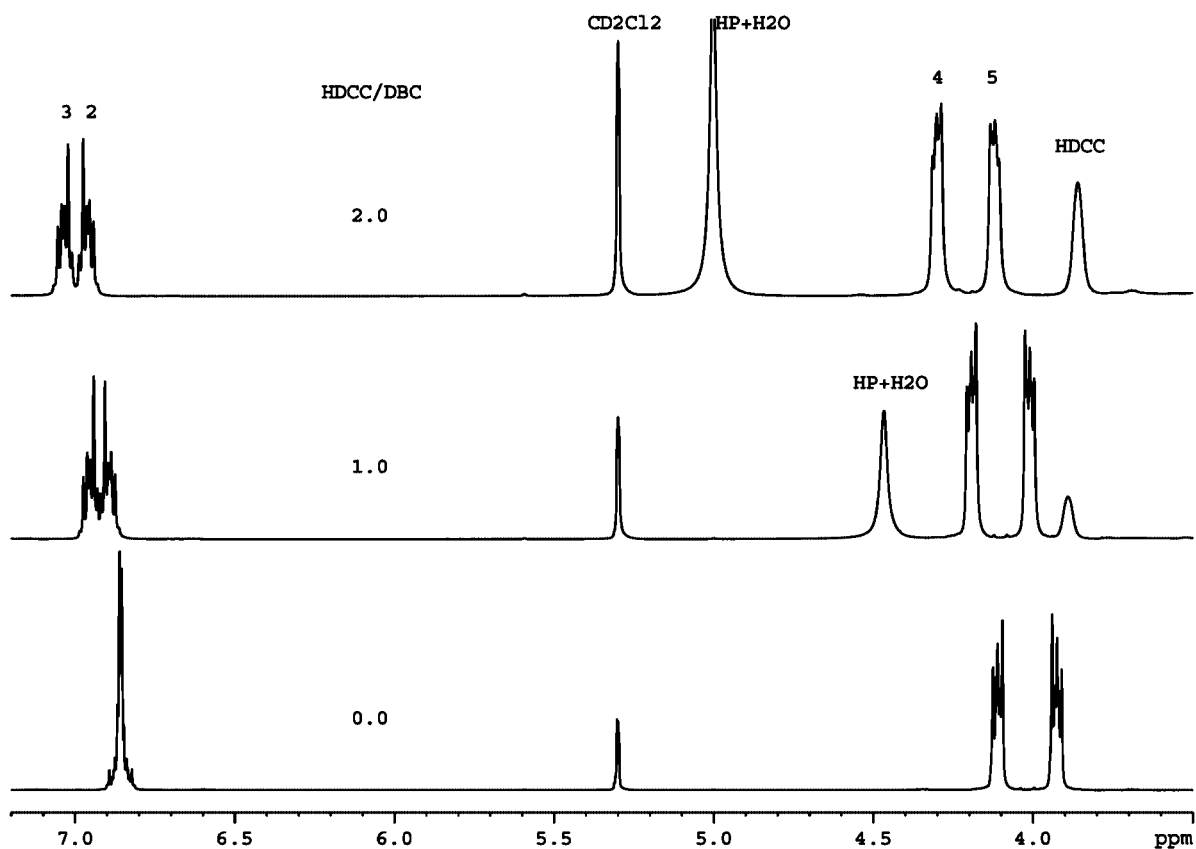


Figure 3. 300.13 MHz ^1H NMR spectra of 0.02 mol/L DBC and its mixtures with indicated amounts of HDCC in CD_2Cl_2 (295 K).

bance intensities between the experimental and calculated spectrum, but one can see a semiquantitative agreement between them. The simulation reproduces the doublet between 1125 and 1150 cm^{-1} and the relative intensity increase of the right band in the complex. In particular, it shows the band characteristic for H_3O^+ -(C-O-C) interaction within the frequency precision limits.

As a whole, one can conclude that FTIR spectra agree with the lowest-energy forms of both DBC and H_3O^+ -DBC complex obtained by DFT calculations reported in the next paragraph.

We also simulated a variant of the complex structure with symmetrically bifurcated hydrogen bonds of H_3O^+ to all of the oxygen atoms of DBC, which is not among the lowest-energy forms of the complex (see below). In the calculated IR spectrum

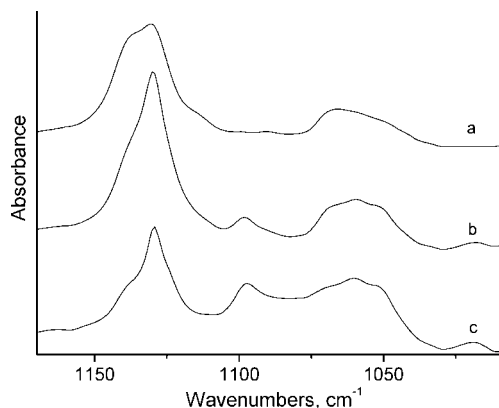


Figure 4. Relevant parts of the FT IR spectra of 0.02 mol/L solution of DBC (a) and its mixtures with 0.02 (b) and 0.04 (c) mol/L HDCC in CD_2Cl_2 .

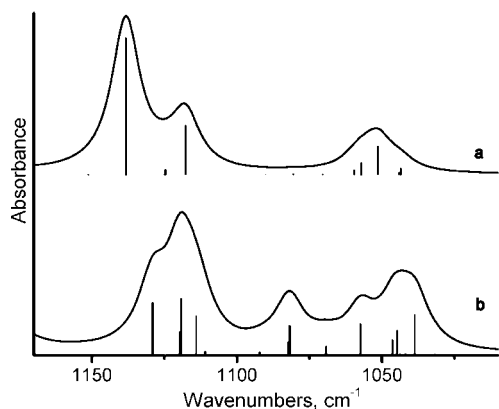


Figure 5. Calculated infrared spectra of DBC (a) and its complex with H_3O^+ (b). Vibrational normal modes were calculated with the B3LYP/6-31G(d) method and the frequencies are scaled by the factor 0.961.

of this form, one normal mode is negative; that is, this structure is a transition state. Its calculated energy 3.8 kcal/mol above the lowest-energy form gives the height of the rotational barrier of H_3O^+ within the complex. With such a low barrier, one can thus expect rather fast (but not ultrafast) rotation of H_3O^+ .

1.3. Quantum Chemical DFT Calculations of the Geometry of DBC and $\text{H}_3\text{O}^+\cdot\text{DBC}$ Complex. It is not very surprising that even DBC alone offers quite a few conformations with energies predicted to be spaced by several kilocalories per mole. Figure 6 shows the most stable two of them.

Structure A is energetically most favored. Structure B corresponds to the conformation detected in the crystal structure, and its energy is higher by 1.88 kcal/mol. Three slightly less stable conformations were found, with relative energies 3.15, 3.29, and 3.46 kcal/mol (the plots of structures along with Cartesian coordinates are given in Supporting Information).

The most stable conformation of the $\text{DBC}-\text{H}_3\text{O}^+$ complex is shown in Figure 7. The structure of the complex with identical conformation of DBC and with the inverted umbrella conformation of H_3O^+ is less energetically favored by 0.34 kcal/mol. Eight more conformational structures were found, two with relative energies 2.7 and 3.1 kcal/mol, the rest in the range 3.9–4.7 kcal/mol. All of them are expectable when considering the relatively flexible C–C and C–O–C junctions in the parts of the molecule not directly involved in the complex bonding. In all of them, there are three strong and linear hydrogen bonds analogous to those in Figure 7, that is, directed to one purely aliphatic ($\text{CH}_2-\text{O}-\text{CH}_2$) oxygen and two partly aromatic ($\text{Ar}-\text{O}-\text{CH}_2$) oxygen atoms. In most of them, the bound H_3O^+

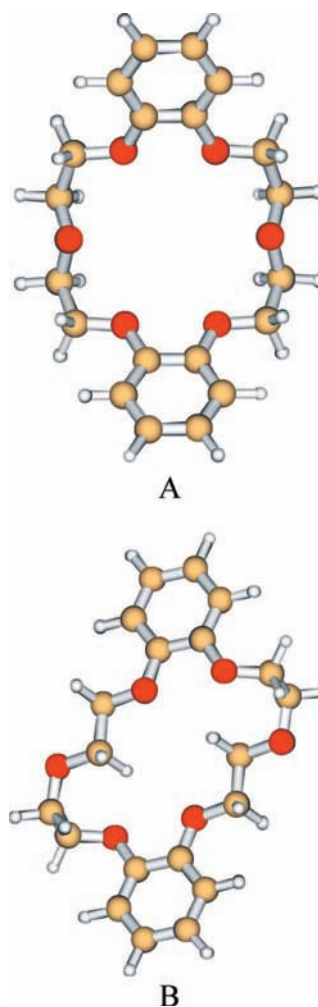


Figure 6. Two most stable conformations of free DBC according to quantum chemical DFT calculation (B3LYP/6-31G(d)).

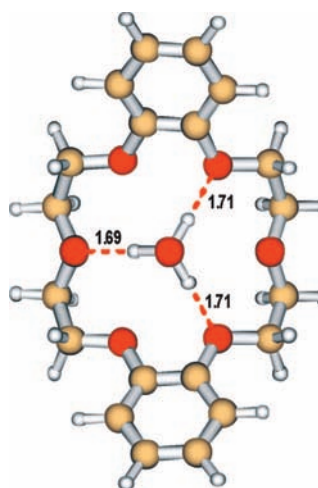


Figure 7. The most stable conformation of a $\text{DBC}-\text{H}_3\text{O}^+$ complex according to quantum chemical DFT calculation (B3LYP/6-31G(d)).

ion itself adopts a slightly pyramidal shape, in agreement with most X-ray structures of the solid $\text{DBC}-\text{H}_3\text{O}^+$ complex.⁹

A mere 60° rotation of the H_3O^+ ion within the molecule leads to a structure completely equivalent to that shown in Figure 7. The barrier of such rotation is⁵ 4–5 kcal/mol, that is, low enough to ensure structure averaging on the NMR time scale even at 295 K. This is the most probable cause of the apparent

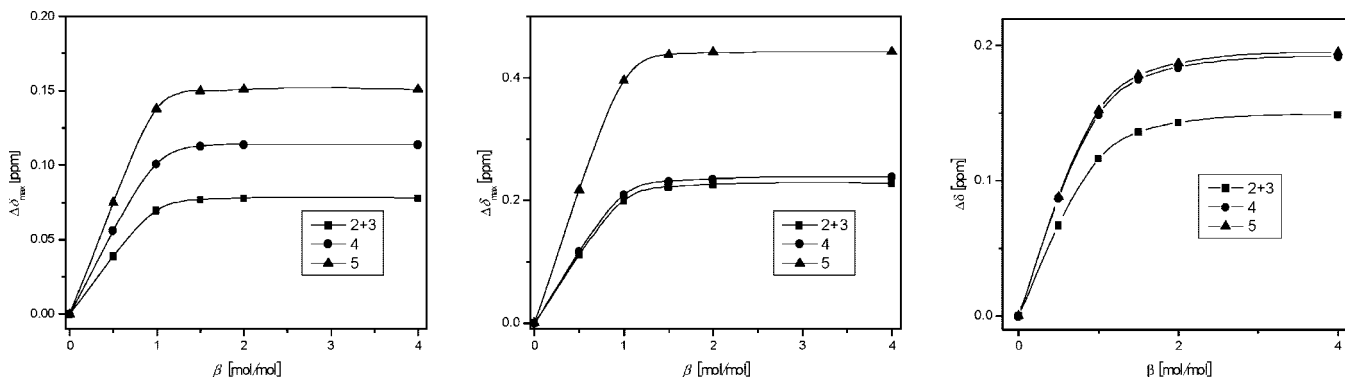


Figure 8. Fitting of experimental values of $\Delta\delta$ of the DBC signals in dependence on β (from left to right) in acetonitrile-*d*₃, nitrobenzene-*d*₅, and CD₂Cl₂ at 295 K.

TABLE 1: Maximal Relative Shifts $\Delta\delta_{\max}$ and Equilibrium Constants^a K Obtained by fitting eq 2 to the Dependences of Experimental Relative Shifts $\Delta\delta$ on β

| signal | nitrobenzene- <i>d</i> ₅ | | acetonitrile- <i>d</i> ₃ | | CD ₂ Cl ₂ | |
|--------|-------------------------------------|----------------------------|-------------------------------------|----------------------------|---------------------------------|----------------------------|
| | $\Delta\delta_{\max}$ (ppm) | K (L·mol ⁻¹) | $\Delta\delta_{\max}$ (ppm) | K (L·mol ⁻¹) | $\Delta\delta_{\max}$ (ppm) | K (L·mol ⁻¹) |
| 2 + 3 | 0.232 | 1.17×10^4 | 0.078 | 1.03×10^4 | 0.153 | 0.655×10^3 |
| 4 | 0.241 | 1.16×10^4 | 0.114 | 1.02×10^4 | 0.197 | 0.659×10^3 |
| 5 | 0.453 | 1.15×10^4 | 0.152 | 1.03×10^4 | 0.200 | 0.651×10^3 |

^a Values ± 2 %rel.

symmetry of the complex in NMR spectra. However, such intramolecular motion does not prevent intermolecular exchange between the bound and free ion (or DBC) which would have the same effect but could be expected to be slower.

2. Equilibrium Constant Measured by NMR. As said above, the shape of spectra under varying HP/DBC molar ratio $\beta < 1.0$ shows that there is a dynamic equilibrium between free DBC and that bound in the complex with HP. By assuming a simple equilibrium expressed by eq 1,

$$K = \frac{[\text{DBC} \cdot \text{HP}]}{[\text{DBC}][\text{HP}]} \quad (1)$$

the relative shift $\Delta\delta$ of a given signal can be expressed^{20,21} by the relation

$$\Delta\delta = \Delta\delta_{\max} \frac{1 + K[\text{DBC}]_0(1 + \beta) - \sqrt{\{1 + K[\text{DBC}]_0(1 + \beta)\}^2 - 4K^2[\text{DBC}]_0\beta}}{2K[\text{DBC}]_0} \quad (2)$$

where $\Delta\delta_{\max}$ is the maximal relative shift corresponding to the pure complex and $\beta = [\text{HP}]_0/[\text{DBC}]_0$. In the following, we identify HP with H₃O⁺, and we assume that $[\text{HP}]_0 = [\text{HDCC}]_0$.

Figure 8 shows fitting of the experimental relative shifts $\Delta\delta$ by eq 2 for acetonitrile-*d*₃, nitrobenzene-*d*₅, and CD₂Cl₂ at 295 K. Its clear success confirms assumptions made, and so does the relative constancy of the fitted value of K for the given medium shown in Table 1.

The value of K in nitrobenzene is found to be 1.16×10^4 L·mol⁻¹, which is 5–10 times lower than that found by electrochemical (half-wave potential³¹ and conductance³²) methods. It is not quite unusual that the values of equilibrium constants established by independent methods differ even by an order of magnitude.³¹ Nonetheless, the gap between our and the earlier reported values deserves some discussion. There is a slight difference between our system containing 3.5 mol H₂O per mol HDCC, that is, 0.07 mol/L H₂O, and that studied by the cited authors, where nitrobenzene was saturated with water, that is, 0.19 mol/L H₂O.¹⁰ Therefore, we repeated our measure-

ments in water-saturated nitrobenzene-*d*₅. Somewhat surprisingly, the larger water content has a slight effect on K , giving the value of 1.56×10^4 L·mol⁻¹. This slight difference, which is probably mostly due to polarizing effect of excess water, does not bridge the gap between our value and those reported earlier,^{31,32} however.

When comparing the respective methods, the present one is more direct and devoid of implicit assumptions. Figure 8 illustrates a remarkably low scatter of experimental points and very successful fitting of eq 2 to them. As seen in Table 1, the chemical shifts of three different signals of DBC give a remarkably similar value of K for each medium. It is also easy to demonstrate¹⁰ that, with $K \geq 10^5$ L·mol⁻¹ (the value reported from conductivity measurement³²), the dependence of $\Delta\delta$ on β must be strictly linear up to $\beta = 1$ where it practically reaches $\Delta\delta_{\max}$ and does not increase any more. This is not so in the case of our data. To get a detectable shift of signals at $\beta > 10$, as we do, one should assume for $K \geq 10^5$ that more than one molecule of H₃O⁺ is bound to DBC. This is physically absurd because just one ion evidently fits into the crown cavity. Moreover, the fitting of eq 2 to the experimental points could not be successful in such a case, contrary to our results. We thus feel justified to assert that the value of K we have found is the right one under the given conditions.

As it can be seen, the value of K in acetonitrile-*d*₃ is similar, although the maximum relative shifts of the signals are quite different. Such similarity can be expected because the two media have very similar dielectric constants (35.6 and 36.6 for nitrobenzene and acetonitrile, respectively). At the same time, both values are much larger than that found in CD₂Cl₂. This must be due to the much better dielectric separation of HP from the DCC⁻ anion in the polar media. In dichloromethane ($\epsilon = 8.93$), a substantial population of an ion pair [H₃O⁺·DCC⁻] strongly influencing the equilibrium can be expected. In such case, eq 1 has a rather formal meaning, and so does the derived value of K .

The fitting of eq 2 to the experimental values of $\Delta\delta$ also offers the extrapolated values of $\Delta\delta_{\max}$, given in Table 1, which

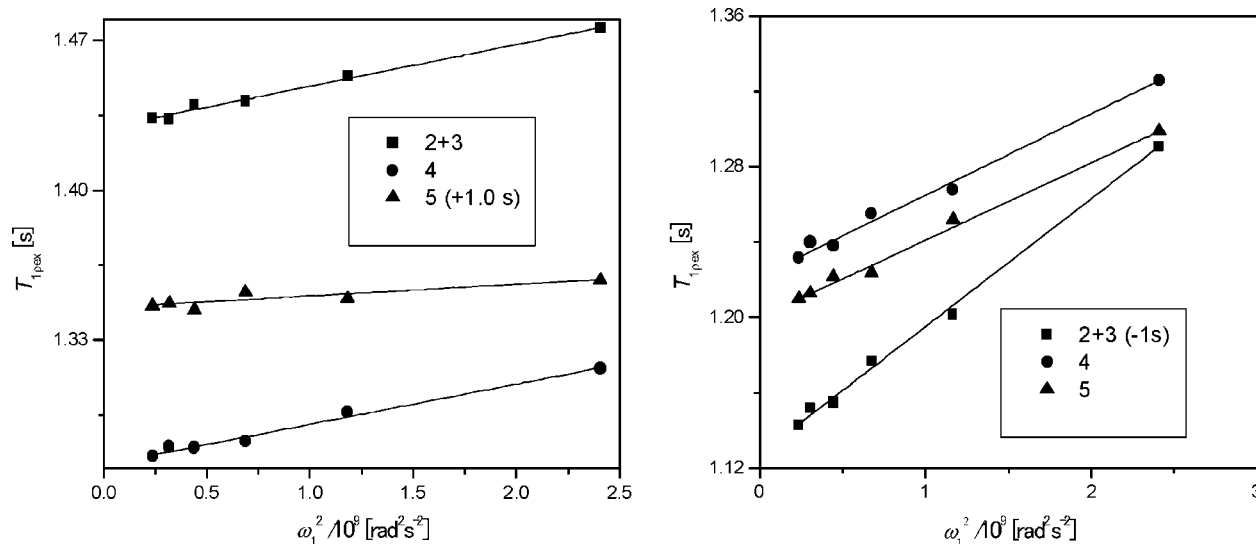


Figure 9. Dependences of $T_{1\text{pex}}$ on the square of spin-lock field intensity ω_1^2 for the individual signals of DBC in its 1:1 mixture with HDCC in nitrobenzene- d_5 (left) and CD_2Cl_2 (right) at 295 K.

TABLE 2: Slopes κ and Abscissas λ of the Dependences of $T_{1\text{pex}}$ on ω_1^2 for Individual Signals of DBC and the Derived Values of τ_{ex} at 295 K

| signal | nitrobenzene- d_5 | | | | CD_2Cl_2 | | | |
|--------|-----------------------|-----------|-------------------------|--------------------------------|--------------------------|-----------|-------------------------|--------------------------------|
| | $\delta\omega^2/10^5$ | λ | $\kappa \times 10^{11}$ | $\tau_{\text{ex}} \times 10^6$ | $\delta\omega^2/10^5$ | λ | $\kappa \times 10^{11}$ | $\tau_{\text{ex}} \times 10^6$ |
| 2 + 3 | 1.881 | 1.429 | 1.956 | 3.68 | 0.832 | 2.127 | 6.792 | 5.65 |
| 4 | 2.048 | 1.272 | 1.875 | 3.84 | 1.380 | 1.222 | 4.297 | 5.93 |
| 5 | 7.201 | 0.345 | 0.558 | 4.02 | 1.422 | 1.200 | 4.121 | 5.86 |

will be utilized in the next section analyzing the exchange dynamics in the system.

3. Exchange Dynamics in the System Measured by NMR.

The changes of NMR spectra under increasing HDCC/DBC ratio shown above leave no doubt about fast exchange between bound and free DBC (or H_3O^+). Nonetheless, the values of T_2 show an apparent lack of the dependence on the delay between the π pulses in the CPMG sequence expected in a case of chemical exchange connected with a marked relative shift of NMR signals.^{20–25} Suspecting a possible masking of the dependence by static dipolar interaction as in the case²⁸ of dibenzo-24-crown-8 with H_5O_2 , we repeated the measurements with the DIFTRE sequence specially designed²⁸ to remove this type of interference. However, the results were quite the same as those with CPMG. Evidently, the DBC• H_3O^+ molecule is already small enough to remove all residual static dipolar interaction by molecular tumbling. Thus, the apparent failure of our measurements had to be due to a high exchange rate.

It is known^{26,27} that faster exchange can sometimes be examined by rotating-frame experiments providing that the spin-lock field is of a sufficiently high intensity. The study reported below was done on the very limit of the abilities of a high-resolution NMR spectrometer, by using an on-resonance pulsed spin-lock with the field intensity ω_1 up to 4.9×10^4 rad/s (the $\pi/2$ pulse being 32 μs) on the robust decoupler coil of a broadband probe. Even then, the slopes of the $T_{1\rho}/\omega_1^2$ dependences were rather low so that usually nine measurements for each point were needed in order to get reasonable data.

It has been shown^{27,20} that the dependence of the exchange part of the rotating-frame relaxation rate on the intensity of the spin-lock field ω_1 (in rad/s) can be expressed as

$$R_{1\text{pex}} = R_{1\rho} - R_2^0 = \alpha(1 - \alpha)\delta\omega^2 \frac{\tau_{\text{ex}}}{1 + \omega_1\tau_{\text{ex}}} \quad (3)$$

where $\delta\omega = 2\pi\Delta\delta_{\text{max}}$ for the given signal and τ_{ex} is the

correlation time of exchange. Equation 3 can be easily transformed into a relation linear in ω_1^2

$$R_{1\text{pex}}^{-1} \equiv T_{1\text{pex}} = \lambda + \kappa\omega_1^2 \quad (4)$$

with

$$\lambda = [\alpha(1 - \alpha)\delta\omega^2\tau_{\text{ex}}]^{-1} \quad (4a)$$

and

$$\kappa = \lambda\tau_{\text{ex}} \quad (4b)$$

Knowing $\delta\omega$, we thus can obtain τ_{ex} either from the slope κ or, less surely, from the abscissa λ . The experimental results for both media are shown in Figure 9, and the extracted values of τ_{ex} are given in Table 2. As shown, the values of τ_{ex} are reasonably constant for different signals under the same conditions, being about 3.8×10^{-6} s in nitrobenzene and 5.8×10^{-6} s in dichloromethane.

The exchange rates in both media are certainly quite fast when considering the substantial energy barrier which the H_3O^+ ion has to cross when jumping from one DBC molecule to another one. It seems inevitable that excess H_2O molecules present in the system must act as a mediator²⁰ of such a process. This possibility is supported by the fast proton exchange between bound H_3O^+ and H_2O evidenced by the fact that both entities have one common signal under all conditions.

As already said above, another dynamics is highly probable in this system, namely, intramolecular rotation of the H_3O^+ ion within the complex. This motion is probably even faster than intermolecular exchange of the ion (although it is not ultrafast, as evidenced by FTIR spectra). However, because each 60° turn of this rotation leads to an equivalent configuration with the same chemical shifts of individual protons, this dynamics cannot be detected by NMR relaxation methods.

Conclusions

By using NMR and IR spectra and ab initio DFT calculations, we have shown that the 1:1 complex of DBC with H₃O⁺ ion has a structure based on three linear hydrogen bonds of H₃O⁺ with one CH₂–O–CH₂ and two Ar–O–Ar oxygen atoms. According to DFT normal-mode calculations, the alternative structure with bifurcated hydrogen bonds to all six oxygen atoms of DBC is a transition state with the energy 3.8 kcal/mol above the ground state. Fast but not ultrafast internal rotation of H₃O⁺ within the complex thus can be expected, thus averaging the complex to an apparently C_{2v} symmetric structure. In addition to this, H₃O⁺ is also swiftly exchanged between the bound and free state, according to NMR rotating-frame relaxation measurements. The correlation time of this exchange was found to be 5.6 × 10⁻⁶ and 3.8 × 10⁻⁶ s in dichloromethane and nitrobenzene, respectively. By using additive relative shifts of the signals in ¹H NMR, the constant of this dynamic equilibrium was found to be 1.16 × 10⁴, 1.03 × 10⁴, and 0.66 × 10³ L·mol⁻¹ in nitrobenzene, acetonitrile, and dichloromethane, respectively. These values are 5–12 times lower than those reported from electrochemical measurements.

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Supporting Information Available: This material is available free of charge via the Internet at <http://pubs.acs.org>.

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