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# Solvent and Ionic Atmosphere Effects in Anion−$\pi$ Interactions: Complexes of Halide Anions with *p*-Benzoquinones

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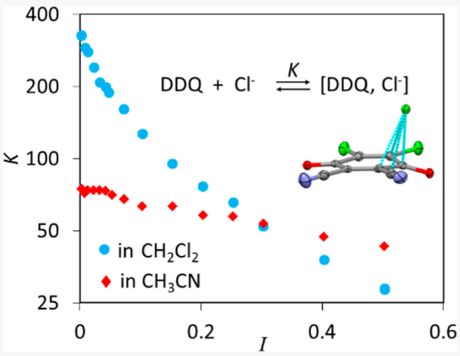
**ABSTRACT:** The interplay between the solvent polarity and ionic atmosphere in anion−$\pi$ association was evaluated via an experimental and a computational study of the BQ·$X^-$ complexes between benzoquinones (BQ) and halide anions ($X^-$). The UV−Vis spectral measurements showed that these complexes are characterized by the strong absorption bands in the 300−450 nm range and their effective formation constants, $K_{eff}$, measured in dichloromethane in the absence (or at low concentrations) of the supporting electrolyte, $Bu_4NPF_6$, were higher than those in acetonitrile. The experimental data were consistent with the results of the computations, which showed that magnitudes of the interaction energy, $\Delta E$, between BQ and $X^-$ decreased considerably with the increase in the polarity of the media. The addition of auxiliary electrolytes (e.g., $Bu_4NPF_6$) led to a decrease in the concentration of the BQ·$X^-$ complexes. These changes were related to the competing associations of the $\pi$-acceptors with halides and $PF_6^-$ anions (since the interaction energies between BQ acceptors and common non-halide anions, e.g., $PF_6^-$, $BF_4^-$, and $NO_3^-$, were comparable to those in the BQ·$X^-$ complexes) and to the increased ionic strength of the solutions. The variations in strength of anion−$\pi$ interactions with the solvent polarity and ionic atmosphere were related to the higher effective ionic radii of the complexes. Due to the larger effects of the auxiliary electrolytes in dichloromethane, the formation constants for the BQ·$X^-$ complexes measured at high ionic strength in this solvent were lower than those in more polar acetonitrile or propylene carbonate. Such a combination of the effects of the solvent and ionic atmosphere should be taken into account when comparing experimental data with the results of the calculations and in design of the systems for molecular recognition and catalysis.




## INTRODUCTION

Anion−$\pi$ bonding represents one of the most fascinating supramolecular interactions that was recognized by a wide chemical community during the last two decades.[1,2] Following computational studies in early 2000,[3−5] which pointed out viability of such counter-intuitive bonding (and earlier observations which were mostly overlooked[6−9]), this bonding was identified experimentally in a large number of chemical and biochemical systems.[10−13] Many recent publications demonstrated high potential of such interactions for anion recognition and transport, catalysis, and other applications.[14−16] Efficient utilization of the anion−$\pi$ bonding and clarification of its major driving forces depend on the elucidation of the effects of internal (properties of the anions and $\pi$-acceptors) and external (medium) factors affecting its strength. Yet, experimental measurements of the anion−$\pi$ complexes remain a challenging task.[17−20] The thermodynamic characteristics of the associations, especially those formed solely by bonding of an anion to the single $\pi$-system (without enhancement by interactions with multiple centers or support of the other forces, e.g., hydrogen bonding) are still scarce. Furthermore, an analysis of the reported data and comparison of various $\pi$-receptors are complicated due to the differences in the solvents in which measurements are carried out. Also, the reported formation constants of anion−$\pi$ complexes were measured mostly via spectral titrations of the solutions of $\pi$-acceptors with the salts of the corresponding anions under conditions of variable ionic strength. Since an ionic atmosphere plays a critical role in the reactions of ionic species[21] and a recent study demonstrated complications in the NMR measurements of the halogen-bonded complexes arising from variations in ionic strength,[22] such an approach raises the question about the accuracy and reliability of the published numbers.

To address these problems, we explore in the current work effects of the solvent and ionic atmosphere on the complex formation between halide anions and neutral $\pi$-acceptors, tetrafluoro- or dichlorodicyano-*p*-benzoquinone (FA and DDQ, respectively, Chart 1). Our recent study demonstrated that interaction of halide anions with these *p*-benzoquinones

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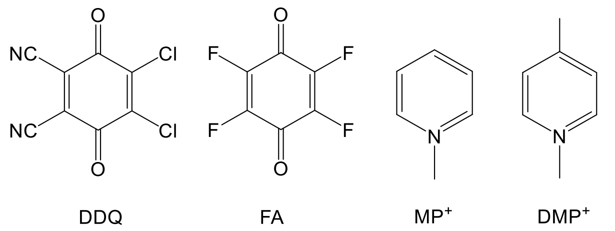
**Chart 1. Structures and Acronyms of the π-Receptors**




(BQs) in acetonitrile resulted in formation of anion−π complexes without interference of hydrogen or halogen bonding, and these processes could be conveniently characterized via UV−Vis measurements.[23] In the current work, we scrutinized how formation of the anion−π complexes is affected by the presence of the other electrolytes. Besides acetonitrile, intermolecular associations were evaluated in dichloromethane and propylene carbonate. These inert aprotic solvents allowed us to evaluate effects of polarity and provided sufficient solubility of ionic and polar substances while minimizing other possible modes of interactions with reactants. To clarify effects of the charge of the π-acceptor in these processes, the association of halide anions with the BQ derivatives was compared to the bonding with cationic methyl-substituted pyridines $MP^+$ and $DMP^+$ (Chart 1).

The primary goal of the current work is to establish and to rationalize effects of the solvent and ionic atmosphere on the formation of anion−π complexes. We also intend to elucidate the impact of the variation of ionic strength in the series of solutions on the accuracy of the measurements of various anion−π associations. These results will facilitate analysis of the reported data and, thus, will help to clarify the nature of anion−π bonding and its dependence on the structural features of interacting species. In addition, they are vital for the choice of the environment for the most effective applications of anion−π interactions.

## ■ EXPERIMENTAL SECTION

Commercially available halide salts ($Bu_4NCl$, $Bu_4NBr$, $Pr_4NBr$, $Bu_4NI$, and $Pr_4NI$), pyridinium salts ($MPPF_6$ and DMPI) and *p*-benzoquinone acceptors (FA and DDQ) were purified by recrystallization and/or sublimation. Dichloromethane and acetonitrile were distilled over $P_2O_5$ under a dry argon atmosphere before use.

Formation constants of the complexes, [BQ, $X^-$], between halides and π-acceptors were established (at 22 °C) using UV−Vis measurements of the solutions containing constant concentrations (from 3 to 10 mM) of the π-acceptor and various concentrations (from 0 to ∼0.6 M) of tetra-*n*-propylammonium or tetra-*n*-butylammonium halide salts (the measurements with $Bu_4NX$ or $Pr_4NX$ afforded essentially the same results). Ionic strength of the solutions, *I*, in the series with constant ionic strength was maintained by addition of $Bu_4NPF_6$ salts. To avoid possible side reactions, the spectra were measured immediately after mixing and measurements involving iodide salts were performed under an argon atmosphere. Formation constants represent averaged values from 3 to 5 series of UV−Vis experiments for each BQ/$X^-$ pair, with each series including 8−10 points. Typically, 500 mkL aliquots of a stock solution of the π-acceptor were mixed with *x* mkL of a stock solution of halide salts (*x* = 30, 60, 100... 500) and (500−*x*) mkL of a solution of $Bu_4NPF_6$ (with the same concentration as halide salt) to keep ionic strength constant throughout the series. In the series with variable *I*, (500−*x*) mkL of pure solvent was added instead of solutions of $Bu_4NPF_6$. As such, the ionic strengths of solutions in such series increased with the increase in concentration of halide salts, which typically varied from 0.02 to 0.5 M.

Effective formation constants for the [BQ, $X^-$] complexes, $K_{eff}$, were calculated via regression analysis of the differential intensities of absorption, ΔAbs (obtained by the subtraction of absorption of components from the absorption of their mixtures) for the series of solutions. These values can be expressed as[23]

$$\begin{aligned}\Delta\text{Abs} &= \varepsilon l \times C_{com}\\ &= \varepsilon l \times \{(C^{o}_{BQ} + C^{o}_{X} + 1/K_{eff})\\ &\quad - ((C^{o}_{BQ} + C^{o}_{X} + 1/K_{eff})^2 - 4C^{o}_{BQ}C^{o}_{X})^{0.5}\}/2\end{aligned} \quad (1)$$

where ε is the difference between extinction coefficients of the complex and π-acceptor at the wavelength used (typically, the wavelength of the maximum of the absorption band of the complex, at which its extinction coefficient was much higher than that of the individual acceptor), *l* is the length of the cell (typically, 1.0 or 2.0 mm), $C_{com}$ is the concentration of the complex, and $C_X{}^o$ and $C_{BQ}{}^o$ are initial concentrations of $X^-$ and BQ, respectively. The fits of the results of the UV−Vis measurements to eq 1 (with ε and $K_{eff}$ as the ajustable parameters) using Origin Pro 2016 are illustrated in Figures S1−S5 in the Supporting Information. It should be mentioned that formation constants of complexes of FA, $MP^+$, and $DMP^+$ with halide anions were rather low (∼1 $M^{-1}$). As such, their reliable measurements required the use of the high concentrations of halide salts (up to about 0.5 M) and therefore the high ionic strength in the series with *I* = const. On the other hand, the formation constants of complexes of DDQ with $Cl^-$ were much higher. As such, they can be measured at lower concentrations of the reactants and lower ionic strength (e.g., 0.1 or 0.02). It also made possible reverse titration in which concentration of chloride was kept constant (i.e., *I* = const without auxiliary electrolyte) and concentration of DDQ was varied. Due to independence of extinction coefficients on ionic strength, the $K_{eff}$ values for complex formation at various *I* values were also obtained as $K_{eff} = C_{com}/[(C_X{}^o - C_{com})(C_{BQ}{}^o - C_{com})]$, where $C_{com} = \Delta\text{Abs}/\varepsilon$ was calculated using values of ε obtained from the measurements of the series of solutions as described above.

In the presence of auxiliary electrolyte, $Bu_4NPF_6$, the π-acceptors form complexes with halide and $PF_6{}^-$ anions with formation constants *K* and $K_A$, respectively. Since spectra of the $BQ{\cdot}A^-$ complex are essentially the same as those of the corresponding π-acceptor, the ΔAbs values can be expressed using eq 2

$$\begin{aligned}\Delta\text{Abs} &= \varepsilon l \times C_{com}\\ &= \varepsilon l \times \{C^{o}_{BQ}C^{o}_{X}/\ (1/\text{K} + C^{o}_{X} + (K_A/K)C^{o}_{A})\}\end{aligned} \quad (2)$$

where $C_A{}^o$ is the concentration of $PF_6{}^-$. The *K* and $K_A$ were evaluated by fits of the absorption data for the series of solutions with *I* = const to this equation (see the Supporting Information for details).

Geometries of the complexes were optimized without constraints via DFT calculations with the M06-2X functional and def2tzvpp basis set using the Gaussian 09 suite of programs.[24,25] Calculations in various solvents were carried out using a polarizable continuum model.[26] The absence of imaginary frequencies confirmed that the optimized structures represent true minima. Earlier computational analysis demonstrated that intermolecular associations are well-modeled using this method.[27] The M06-2X functional provided most reliable results among a number of density functionals in analysis of anion−$\pi$ interactions.[28] The def2tzvpp basis set that was used in this work does not include diffuse functions since previous computational analysis demonstrated that very similar results were obtained in modeling of noncovalent interactions involving anions with the triple-$\zeta$ basis sets with and without diffuse functions.[29] Besides, our previous studies confirmed that such calculations (with acetonitrile as a medium) reproduced well characteristics of the anion−$\pi$ complexes between (pseudo-)halide ions and *p*-benzoquinone acceptors.[23,30] Values of $\Delta E$ were determined as follows: $\Delta E = E_c - (E_{BQ} + E_X)$, where $E_c$, $E_{BQ}$, and $E_X$ are sums of the electronic and ZPE of the optimized complex, BQ, and anion. Characteristics of the complexes are listed in the Supporting Information.

## RESULTS AND DISCUSSION

An addition of tetraalkylammonium halide salts, $Alk_4NX$ (Alk = *n*-propyl or *n*-butyl, X = $Cl^-$ or $Br^-$) to the solutions containing DDQ or FA led to the appearance of new absorption bands, indicating formation of the anion−$\pi$ complexes (Figures 1 and S1, S2 in the Supporting Information).[23] In the current work, formation constants of these complexes were first evaluated via quantitative treatment of the dependence of intensity of new bands on the concentrations of halides in the series of solutions with constant concentration of the $\pi$-acceptor. These measurements were performed using two types of series: (i) solutions containing only acceptors and halide salt, so their ionic strength varied due to the changes in concentration of the halide salt from about 0.005 to 0.5 M and (ii) solutions with constant ionic strengths, which was maintained by the auxiliary electrolyte, $Bu_4NPF_6$. The latter was chosen based on the computational analysis of interaction of the $\pi$-acceptors from Chart 1 with various anions (vide infra). Importantly, an addition of $Bu_4NPF_6$ to the solutions of an individual BQ acceptor resulted only in a very small blueshift of the absorption band of the latter (Figure 1).

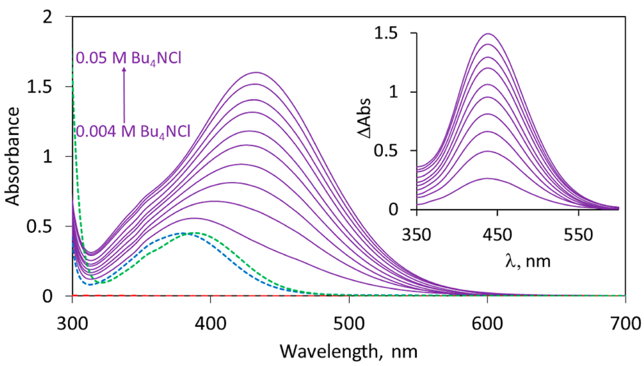



**Figure 1.** Spectra of the dichloromethane solutions (solid violet lines) with constant concentration of DDQ (2.5 mM) and variable concentrations of $(Pr_4N)Cl$. Ionic strength of solutions was maintained constant ($I$ = 0.5) using the auxiliary electrolyte, $Bu_4NPF_6$. Dashed green and red lines show spectra of individual DDQ and $Pr_4NCl$, and dashed blue lines show the spectrum of solution of 2.5 mM DDQ and 0.5 M $Bu_4NPF_6$. Insert: absorption of the DDQ·$Cl^-$ complex obtained by the subtraction of the absorption of individual components from the absorption of their mixtures.

For both types of series, the intensities of the absorption of the anion−$\pi$ complexes ($\Delta$Abs), obtained by the subtraction of the absorption of individual DDQ and $(Pr_4N)Cl$ from the absorption of their mixtures, were well-fitted using eq 1 corresponding to the 1:1 binding isotherm for equilibrium in eq 3 (Figures 2, S1 and S2 in the Supporting Information)

$$BQ + X^- \rightleftarrows BQ{\cdot}X^- \tag{3}$$

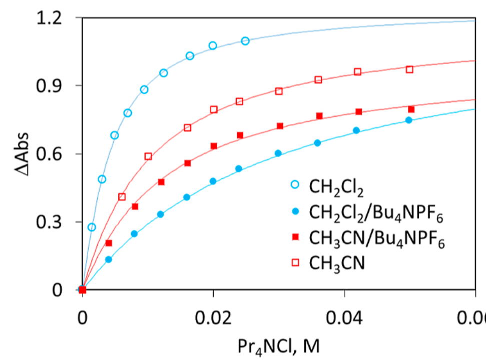



**Figure 2.** Variations in the absorbance ($\Delta$Abs) of the DDQ·$Cl^-$ complex with concentrations of $Pr_4NCl$ in solutions with 2.5 mM DDQ in $CH_2Cl_2$ or $CH_3CN$ with constant ionic strength $I$ = 0.5 (maintained by $Bu_4NPF_6$) or variable ionic strength (no supplementary electrolyte), as indicated. Solid lines show fitting of $\Delta$Abs to the 1:1 binding isotherm (see the Experimental Section for details).

The *effective* formation constants of the complexes, $K_{eff}$, for such fitting were defined as follows

$$K_{eff} = C_{com}/\{(C^{o}_{BQ} - C_{com})(C^{o}_{X} - C_{com})\} \tag{4}$$

where $C_{com}$ is the concentration of the complex, and $C_X{}^o$ and $C_{BQ}{}^o$ are the initial concentrations of $X^-$ and BQ, respectively. The values of $K_{eff}$ obtained from the treatment of the data (see the Experimental Section for details) measured under conditions of constant and variable ionic strength are listed in Table 1.

Overall, the fitting of the UV−Vis absorbance of anion−$\pi$ complexes to the 1:1 binding isotherm produced seemingly impeccable results for all series of measurements (i.e., with constant or variable ionic strength, Figures 2, and S1 and S2 in

**Table 1. Effective Formation Constants of the Anion−$\pi$ Complexes, $K_{eff}$**

| | $K_{eff}$ (acetonitrile), $M^{-1}$ | | $K_{eff}$ (dichloromethane), $M^{-1}$ | |
|---|---|---|---|---|
| complex | constant IS[a] | variable IS[b] | constant IS[a] | variable IS[b] |
| DDQ·$Cl^-$ | 45 ± 5 | 75 ± 10[c] | 32 ± 3 | 350 ± 30 |
| FA·$Br^-$ | 1.3 ± 0.2 | 2.6 ± 0.5[c] | 0.2 ± 0.1 | 2.3 ± 0.2 |
| MP+·$Br^-$ | 1.4 ± 0.2 | 4.8 ± 0.4 | n/a | n/a |
| DMP+·$I^-$ | 0.6 ± 0.1 | 5.6 ± 0.5 | n/a | n/a |
| DMP+·$Br^-$ | 1.6 ± 0.3 | 4.6 ± 0.4 | n/a | n/a |

[a]Maintained at $I$ = 0.5 by $Bu_4NPF_6$. [b]Ionic strength varied in series of measurements with the changes in concentration of halide salt (typically from 0.005 to 0.5 M). [c]From ref 23.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the Supporting Information). The treatment of the absorption data using the Benesi–Hildebrandt method[31] (which is also commonly applied for evaluation of formation constants and extinction coefficients of various intermolecular complexes) produced straight lines with high $R^2 > 0.99$ (Figures S1 and S2 in the Supporting Information). However, the dependencies of the ΔAbs on [$Pr_4NCl$] measured in dichloromethane in the presence of auxiliary electrolyte, $Bu_4NPF_6$ (under conditions of constant ionic strength), and in the absence of the supporting electrolyte (i.e., under conditions of variable ionic strength) were quite different (Figure 2). Accordingly, the $K_{eff}$ values resulting from the fitting of the absorption data in the series of dichloromethane solutions with variable ionic strength were about 10 times higher than those measured under conditions of constant ionic strength. In acetonitrile, the distinctions between the series measured in the presence and in the absence of $Bu_4NPF_6$ were less pronounced (Figure 2). The effective formation constants of the anion–$\pi$ complexes of neutral $\pi$-acceptors resulting from the measurements in this polar solvent in the presence of $Bu_4NPF_6$ (constant ionic strength) were about 35–50% lower than those obtained from the variable ionic strength study.

For the complexes of halide anions with cationic $MP^+$ and $DMP^+$ $\pi$-receptors, the $K_{eff}$ values obtained by the fitting of the absorption data for the series of experiments with variable ionic strengths were also 3–10 times higher than those resulting from the series in which ionic strength was kept constant (Table 1, Figures S3 and S4 in the Supporting Information).

The $K_{eff}$ values for the $DDQ{\cdot}Cl^-$ complex measured in dichloromethane at constant, but lower ionic strengths (maintained by $Bu_4NPF_6$) were substantially higher than those measured at $I = 0.5$. In particular, fitting of the absorption data measured at $I$ of 0.1 and 0.02 produced $K_{eff}$ values of 130 and 250 $M^{-1}$, respectively. The formation constants measured in the series of solutions with constant concentration of $Pr_4NCl$ and variable concentration of DDQ (in which constant ionic strength was maintained without addition of auxiliary electrolyte, see Figure S5 in the Supporting Information) were consistent with those measured in the presence of $Bu_4NPF_6$ ($K_{eff} = 130$ $M^{-1}$ and 240 $M^-$ at $I =$ 0.1 and 0.02, respectively). The extinction coefficients of the complexes obtained from the series with different concentrations of added $Bu_4NPF_6$ salt or without auxiliary electrolyte were about $5 \times 10^3$ $M^{-1}$ $cm^{-1}$. It indicates that while the ionic strength (and the presence of $Bu_4NPF_6$) had a substantial effect on the formation constants, its effect on the extinction coefficients of the complexes was relatively minor, if any. The invariance of the extinction coefficients allowed us to evaluate concentration of the complexes and therefore their effective formation constant in solutions with a wide range of ionic strength, $I$. The latter was adjusted by the variation of concentration of $Bu_4NPF_6$ in the solutions with constant concentrations of BQ acceptors and halide anions (see the Experimental Section for the details). The resulting dependencies of $K_{eff}$ on $I$ measured for the $DDQ{\cdot}Cl^-$ complex are illustrated in Figure 3 (the dependencies for the $FA{\cdot}Br^-$ complex follows analogous trends, see Figure S6 in the Supporting Information).

A glance at Figure 3 indicates that the increase in the ionic strength of the solutions, $I$, is accompanied by the decrease in the effective formation constant of the anion–$\pi$ complexes. The most pronounced variations of the $K_{eff}$ values are observed in moderately polar dichloromethane (dielectric constant $\varepsilon_r$ = 8.9). In this solvent, $K_{eff}$ for the $DDQ{\cdot}Cl^-$ complex measured at $I = 0.0025$ (which was determined from the concentration of $Bu_4NCl$, with no $Bu_4NPF_6$ added) is about an order of magnitude higher than that measured at $I = 0.5$ (in which concentration of $PF_6^-$ was 0.475 M). In more polar acetonitrile ($\varepsilon_r$ = 37.5), the $K_{eff}$ values measured at the lowest ionic strength were about twice as large as those measured at the highest ionic strength. Finally, in the very polar propylene carbonate solvent ($\varepsilon_r$ = 64.9), only about 10% decrease in the values of $K_{eff}$ was observed when ionic strength decreased from $I = 0.025$ to $I = 0.5$. It is also noticeable that the variation in ionic strength results in a switch of the relative values of the effective formation constants in the solvents of low and high polarity. Indeed, the values of $K_{eff}$ measured at high ionic strength in dichloromethane are lower than those measured under analogous conditions in more polar acetonitrile or propylene carbonate. However, due to a much steeper increase in $K_{eff}$ with a decrease in $I$ in dichloromethane, the $K$ values measured in this solvent at low ionic strength are much higher than those determined in acetonitrile (and propylene carbonate).

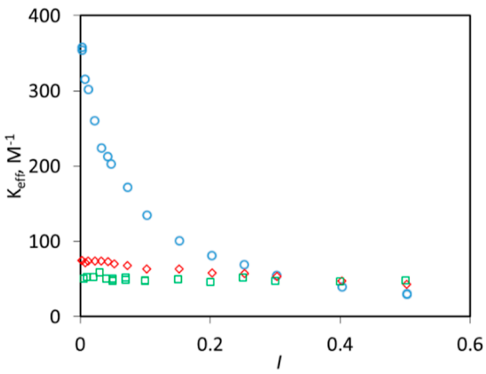


**Figure 3.** Dependencies of the effective formation constants of $DDQ{\cdot}Cl^-$ complexes on ionic strength (adjusted by $Bu_4NPF_6$) in dichloromethane (blue ○), acetonitrile (red ◊), and propylene carbonate (green □).

In general, the variations of the $K_{eff}$ values in Figure 3 in various solvents can be related to the competing associations of the $\pi$-acceptors with the halide and $PF_6^-$ anions and to the changes in the activities of ionic species involved in eq 3 with the ionic strength of the solutions (i.e., to the specific and non-specific action of the auxiliary electrolyte). To clarify solvent and supplementary electrolyte effects, we turned to the computational analysis of anion–$\pi$ complexes under study. The complexes and their components were optimized without constraints in various media using M062x/def2tzvpp calculations and the PCM solvation model (see the Experimental Section for details).[25,26] Typical geometries of the complexes resulting from the optimization of the $DDQ{\cdot}Cl^-$ and $FA{\cdot}Br^-$ complexes are illustrated in Figure 4.

Regardless of the solvent, general features of these structures are similar to those observed in the corresponding experimental solid-state (X-ray) structures and to the structures calculated earlier in acetonitrile.[23] In all cases, the halides are located over the BQ ring, almost atop the carbonyl carbon. Both complexes showed some increase in the separations between anions and $\pi$-acceptors with the increase in the polarity of media. Specifically, the $X^-{\cdots}C$ distances were about 10–15% larger in the optimized $FA{\cdot}Br^-$ and $DDQ{\cdot}Cl^-$

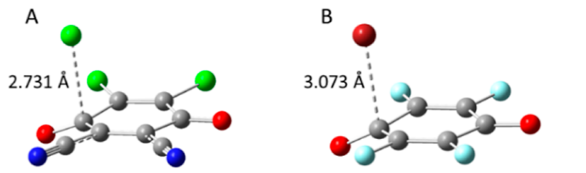


**Figure 4.** Structures of the DDQ·Cl$^-$ (A) and FA·Br$^-$ (B) complexes resulted from the M062x/def2tzvpp optimization with dichloromethane as a medium (dashed lines and numbers indicate the shortest interatomic separations between anions and $\pi$-acceptors).

pairs in the polar solvents as compared to those in vacuum (Figure 5).

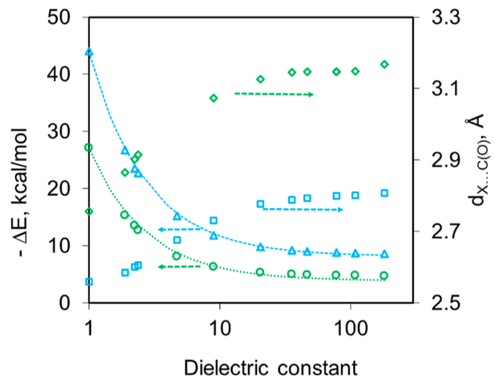


**Figure 5.** Dependencies of $\Delta E$ for FA·Br$^-$ (green ○) and DDQ·Cl$^-$ (blue Δ) pairs and $d_{X\cdots C(O)}$ in FA·Br$^-$ (green ◊) and DDQ·Cl$^-$ (blue □) pairs on the dielectric constant (see Table S1 in the Supporting Information for details; note that dashed lines represent fit of variations of interaction energies with $\varepsilon_r$ using the Born model, see eq 6).

The changes in the interaction energies with polarity of the medium were more pronounced (Figure 5). The $\Delta E$ values for the FA·Br$^-$ and DDQ·Cl$^-$ complexes calculated in vacuum were about −44 and −27 kcal/mol, respectively. The magnitudes of $\Delta E$ decreased sharply as the values of the dielectric constants increased from 1 to 10. At larger $\varepsilon_r$, the changes in $\Delta E$ were smaller, and these values were almost constant for the polar solvents with $\varepsilon_r > 30$ (about −5 and −9 kcal/mol for the FA·Br$^-$ and DDQ·Cl$^-$, respectively, see Table S1 in the Supporting Information for details).

The variations in $\Delta E$ are apparently related to the larger effective ionic radii of the anionic $\pi$-complex (in which one side of the anion is covered with the neutral $\pi$-acceptor) as compared to the individual halides, which leads to the different solvation energies of these ionic species. According to the Born model, free energy of solvation is approximated as follows

$$\Delta G = -N_A z^2 e^2/(8\varepsilon_0 r) \times (1 - 1/\varepsilon_r) \quad (5)$$

where $N_A$ is the Avogadro number, $z$ and $e$ are the charge of an ion and the elementary charge, respectively, $\varepsilon_0$ is permittivity of vacuum, $r$ is effective radius of the ion, and $\varepsilon_r$ is the dielectric constant of the solvent.[32,33] Assuming that the changes in $\Delta E$ are determined by the variations in the solvation energies of the anion−$\pi$ complex and the free halide anion (both with $z$ = 1) and that the effective radii of the anionic species, $r_\pi$ and $r_X$, remain approximately constant, the $\Delta E$ values in different solvents can be expressed as follows

$$\Delta E = \Delta E^v - N_A e^2/(8\varepsilon_0) \times (1 - 1/\varepsilon_r)(1/r_\pi - 1/r_X) \quad (6)$$

where $\Delta E^v$ represents the value calculated in vacuum. The dashed lines in Figure 5 show variations of $\Delta E$ with $\varepsilon_r$ for both DDQ/Cl$^-$ and FA/Br$^-$ pairs obtained by the fitting of the calculated values with the effective radii of halides $r_X$ and anion−$\pi$ complexes $r_\pi$ as adjustable parameters. The good fit obtained with $r_X$ = 2.00 Å and $r_\pi$ = 2.55 Å for FA/Br$^-$ pairs and $r_X$ = 1.85 Å and $r_\pi$ = 2.13 Å for DDQ/Cl$^-$ pairs confirms that variations of the strength of anion−$\pi$ complexes in various media are well accounted by the Born model.

To choose an auxiliary electrolyte and to clarify its effects, we also evaluate the associations between the $\pi$-acceptors and $PF_6^-$, $SO_4^{2-}$, $BF_4^-$, $ClO_4^-$, and $NO_3^-$ anions, which represent anionic components of the common supporting electrolytes. Structural features of the optimized complexes are illustrated in Figure 6.

Similar to the results of the previous X-ray structural and theoretical analyses of the anion−$\pi$ interaction involving $[MX_n]^{m-}$ anions,[34,35] the binding mode of the trigonal planar

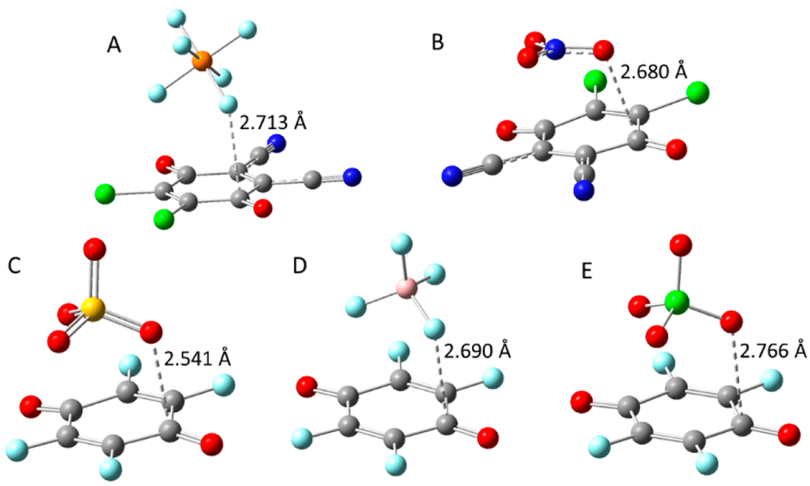


**Figure 6.** Structures of the DDQ·PF$_6^-$ (A), DDQ·NO$_3^-$ (B), FA·SO$_4^{2-}$ (C), FA·BF$_4^-$ (D), and FA·ClO$_4^-$ (E) complexes resulted from the M062x/def2tzvpp optimizations with dichloromethane as a medium (dashed lines and numbers indicate the shortest interatomic separations between anions and $\pi$-acceptors).

$NO_3^-$ molecule resembles a stacking interaction. For tetrahedral $BF_4^-$, $ClO_4^-$, and $SO_4^{2-}$ and octahedral $PF_6^-$ anions, the most favorable orientation is the one with three F (or O) atoms pointing toward the ring. Interaction energies and the normalized shortest interatomic separations in these complexes in comparison with the characteristics of the complexes with halides are listed in Table 2. In accordance

**Table 2. Calculated Characteristics of the Anion−π Complexes**

| | | acetonitrile | | dichloromethane | |
|---|---|---|---|---|---|
| π-acceptor | anion | $\Delta E$, kcal/mol[a] | $R_{XC}$[b] | $\Delta E$, kcal/mol[a] | $R_{XC}$[b] |
| DDQ | $Cl^-$ | −9.24 | 0.81 | −11.83 | 0.79 |
| | $PF_6^-$ | −6.86 | 0.87 | −8.43 | 0.86 |
| | $BF_4^-$ | −8.51 | 0.84 | −10.04 | 0.83 |
| | $NO_3^-$ | −11.19 | 0.84 | −12.83 | 0.85 |
| FA | $Br^-$ | −5.05 | 0.89 | −6.32 | 0.87 |
| | $PF_6^-$ | −5.56 | 0.89 | −6.32 | 0.88 |
| | $BF_4^-$ | −6.81 | 0.85 | −7.80 | 0.85 |
| | $SO_4^{2-}$ | −15.65 | 0.80 | −16.11 | 0.80 |
| | $NO_3^-$ | −8.41 | 0.85 | −9.44 | 0.86 |
| | $ClO_4^-$ | −7.15 | 0.86 | −8.14 | 0.86 |
| $DMP^+$ | $Br^-$ | −5.31 | 1.01 | | |
| | $I^-$ | −4.79 | 1.04 | | |
| | $PF_6^-$ | −4.92 | 0.99 | | |

[a] $\Delta E = E_C - (E_{BQ} + E_X)$, where $E_C$, $E_{BQ}$, and $E_X$ are sums of the electronic and ZPE of the optimized complex, BQ, and anion, respectively. [b] $R_{XC} = d_{XC}/(r_X + r_C)$, where $d_{XY}$ is the shortest interatomic distances in the complexes and $r_X$ and $r_y$ are van der Waals radii of the interacting atoms.

with the observed formation constants, the magnitude of the interaction energies in the DDQ·$Cl^-$ complex is higher than that in FA·$Br^-$. The most notable, however, is the fact that the magnitudes of the interaction energies between π-acceptors and the $PF_6^-$, $BF_4^-$, $SO_4^{2-}$, and $NO_3^-$ anions are comparable or higher than those in the corresponding complexes with the halides.

The quantum theory of atoms in molecules (QTAIM) analysis[36] suggests that strong interaction in complexes with polyatomic anions is related to the multicenter interactions of π-acceptors with these anionic species. Indeed, all of them show two or three bond paths and corresponding (3, −1) bond critical points (BCPs) as compared to the one bond path with one (3, −1) BCP in each complex with halide anions (Figure S15 in the Supporting Information).

The complexes of each acceptor with various anions also showed similar contractions of the interatomic separations as compared to the sum of the van der Waals radii. In the complexes of the cationic π-acceptor, $DMP^+$, the $R_{XY}$ values were about 1.0 (i.e., the interatomic distances were close to the van der Waals separations), regardless of the anion. These features are also consistent with the comparable strength of bonding in the complexes with halide and non-halide anions.

Although the $\Delta E$ and $R_{XC}$ values for the complexes of each π-acceptor with halides and non-halide anions were similar, their UV−Vis spectral characteristics were quite different. In agreement with the experimental data, the TD DFT calculations revealed that the complexes with halides were characterized with the new absorption bands in the UV range (Table 3), which were not present in the spectra of the individual components. The calculated energies of the

**Table 3. Exprimental and Calculated Spectral Characteristics of the Anion−π Complexes[a]**

| | | $\lambda_{max}$, nm | | $\varepsilon \times 10^{-3}$, $M^{-1}cm^{-1}$ | |
|---|---|---|---|---|---|
| complex | solvent | exp | calc[a] | exp | calc[a] |
| DDQ·$Cl^-$ | $CH_3CN$ | 437 | 403 | 4.5 | 6.9 |
| | $CH_2Cl_2$ | 438 | 415 | 5.5 | 7.3 |
| FA·$Br^-$ | $CH_3CN$ | 438 | 418 | 3.2 | 4.3 |
| | $CH_2Cl_2$ | 440 | 427 | 3.5 | 5.8 |
| DMP+·$Br^-$ | $CH_3CN$ | 271 | 270 | 2.0 | 0.6 |
| $DMP^+$·$I^-$ | $CH_3CN$ | 323 | 315 | 1.5 | 0.8 |

[a] From TD DFT M06-2X/def2tzvpp calculations.

absorption band maxima of anion−π complexes were, on average, within 0.15 eV of the corresponding experimental values, and the average absolute differences between calculated and experimental log ε were about 0.3. In contrast to the complexes with halides, the spectra of the complexes with $PF_6^-$ anions obtained from the TD DFT calculations were very close to those of the individual π-acceptor (they contained no new bands with $\lambda > 200$ nm). For example, the calculated DDQ·$PF_6^-$ complexes showed bands with the maximum at about 372 nm, as compared to $\lambda_{max} = 380$ nm for the DDQ molecule (with ε of about 900 $M^{-1}$ $cm^{-1}$ in all cases). These results were consistent with the experimental measurements, which showed a small blueshift of the absorption band of DDQ upon addition of $PF_6^-$ anions (Figure 1). The calculated spectra of the complexes of DDQ with the other non-halide anions (and those of the complexes of $PF_6^-$ with FA and $DMP^+$) were also similar to the spectra of the individual acceptors, in accordance with the experimental data which show essentially the same absorbance of the solutions of DDQ in the presence and absence of these anions (Figure S7 in the Supporting Information). This suggests that although charge transfer plays a vital role in formation of the BQ complexes with halides, it is probably negligible in the complexes with the auxiliary anions considered in the current work.

The data in Table 2 indicate that the complexes of π-acceptors with $PF_6^-$ are characterized by the lower magnitudes of $\Delta E$ as compared to those with the other anions ($BF_4^-$, $NO_3^-$, etc.), which are commonly used in supporting electrolytes. These results were supported by the experimental measurements which showed that addition of $Bu_4NPF_6$ resulted in a smaller decrease in the concentration of the DDQ·$Cl^-$ complex as compared to addition of the salts with the other anions (Figure S7 in the Supporting Information). As such, the $Bu_4NPF_6$ salt was chosen to maintain ionic strength in the series of the solutions with various concentrations of halide salts (vide supra). The difference between interaction energies of the $PF_6^-$ and $Cl^-$ anions with DDQ suggests that the formation constants of DDQ·$Cl^-$ complexes are roughly 50−300 times higher than those of DDQ·$PF_6^-$ (see the Supporting Information for the details). As such, the latter is present in the solutions with a high concentration of $Bu_4NPF_6$. The $\Delta E$ values (and therefore formation constants) for FA·$Br^-$ and FA·$PF_6^-$ complexes are comparable (Table 3). This suggests a more substantial effect of addition of $PF_6^-$ on the formation of complexes of $Br^-$ with FA. Furthermore, computational analysis indicated that interaction of halides with the π-acceptor associated with $PF_6^-$ is much weaker than that with the individual DDQ or FA, that is, the presence of the triple $PF_6^-$·FA·$Br^-$ and $PF_6^-$·DDQ·$Cl^-$ complexes (Figure S9 in the Supporting Information) in solutions can be


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neglected. Thus, evaluation of the formation constants of complexes with halides should take into account a decrease in the equilibrium concentration of the $\pi$-acceptors due to their association with $PF_6^-$ as follows

$$K = C_{com}/\{(C_{BQ}^{o} - C_{com} - C_{CA})(C_{X}^{o} - C_{com})\} \tag{7}$$

where $C_{CA}$ is concentration of the complex between $\pi$-acceptors and $PF_6^-$, which is determined by the concentration of $PF_6^-$ in the solutions, $C_A$, and the formation constants of their complexes with the $\pi$-acceptor, $K_A$. Since the UV−Vis spectra of $BQ{\cdot}PF_6^-$ complexes are very close to those of the individual acceptors, the variations of ΔAbs in the series of solutions containing halides and $PF_6^-$ can be expressed using eq 2 (see the Experimental Section and the Supporting Information for details). The fitting of the experimental absorption data using eq 2 (which takes into account competing formation of both types of complexes, see Figures S9−S13 in the Supporting Information) produced values of $K$ (and $K_A$) which are listed in Table 4.

**Table 4. Formation Constants, $K$, of the Complexes with Halides Evaluated in the Presence of $Bu_4NPF_6$ ($I$ = 0.5) Considering Formation of the Complexes with $PF_6^-$ (with Formation Constants $K_A$ Shown in the Parentheses)[a]**

| complex | $CH_3CN$ | $CH_2Cl_2$ |
|---|---|---|
| $DDQ{\cdot}Cl^-$ | 67 ± 10 (0.3) | 36 ± 5 (0.3) |
| $FA{\cdot}Br^-$ | 2.0 ± 0.5 (1.5) | 1.9 ± 0.5 (1.5) |
| $DMP^+{\cdot}I^-$ | 3.2 ± 1.0 (2.2) | |
| $DMP^+{\cdot}Br^-$ | 3.0 ± 1.0 (0.7) | |

[a]In $M^{-1}$.

Comparison of the data in Tables 4 and 1 shows that the explicit consideration of the complexes with $PF_6^-$ produced higher $K$ values as compared to the corresponding $K_{eff}$ measured in the presence of auxiliary electrolyte. Since the interaction of DDQ with $Cl^-$ is much stronger than that with $PF_6^-$ (so relative concentrations of the $DDQ{\cdot}PF_6^-$complexes are low), the $K$ values are close to $K_{eff}$ evaluated neglecting the formation of the complexes with $PF_6^-$. The values of $K$ for the $DDQ{\cdot}Cl^-$ complex decrease with the increase in the ionic strength of solutions (Figure S14 in the Supporting Information) in a similar way as $K_{eff}$ (Figure 3). It indicates that besides the specific effect of $PF_6^-$ (related to its association with the $\pi$-acceptor), the ionic strength of solutions also affects formation of anion−$\pi$ complexes with halides. Indeed, equilibrium constants determined from the concentrations of reagents and products, such as $K$, represent a product of thermodynamic (invariant) constants $K^o$ and media-dependent activity coefficients, $\gamma$[37,38]

$$K = K^{o}\gamma_{\pi}/\gamma_{BQ}\gamma_{X} \tag{8}$$

where $\gamma_\pi$, $\gamma_{BQ}$, and $\gamma_X$ are activity coefficients of the complex, BQ, and $X^-$, respectively. In the framework of the extended Debye−Hückel theory, the activity coefficients of ionic species are expressed as follows

$$\log \gamma = AI^{0.5}/(1 + B\mathring{a}I^{0.5}) \tag{9}$$

where $\mathring{a}$ is the effective counterion separation and $A$ and $B$ are coefficients determined from the dielectric constants of the solvent and the temperature [$A = 1.8246 \times 10^6/(\varepsilon_r T)^{1.5}$ and $B = 50.2904/((\varepsilon_r T)^{0.5}]$.[33,39] Thus, the variation of K with $I$ is expressed as follows

$$\log K = \log K^{o} - ABI(\mathring{a}_\pi - \mathring{a}_X)/((1 + B\mathring{a}_\pi I^{0.5})(1 + B\mathring{a}_X I^{0.5})) \tag{10}$$

where $\mathring{a}_\pi$ and $\mathring{a}_X$ are separations of counterions involving anion−$\pi$ complexes and free halide anions, and the changes in the activity coefficients of the neutral species with the ionic strength are neglected. Since the $\pi$-acceptor covers one side of the anion in the anion−$\pi$ complexes, the effective counterion separations involving such species are, on average, larger than those involving free anions. In other words, both solvent and ionic strength dependencies are apparently related to the increase in the effective ionic radii of the complexes as compared to those of the individual halide anions. Application of eq 10 (with $\mathring{a}_\pi$ and $\mathring{a}_X$ values as adjustable parameters) allows to account for the variations of the $K$ values with ionic strength in acetonitrile and dichloromethane (Figure S14 in the Supporting Information), which supports this interpretation.

## ■ CONCLUSIONS

The results of the current work allowed us to clarify the effects of solvent polarity and ionic strength on the formation of anion−$\pi$ complexes between neutral $\pi$-acceptors and halide anions. First, the formation of such complexes is facilitated by the non-polar environments with low ionic strength. This conclusion is supported by the substantially higher equilibrium constants of complex formation measured in the absence or with low concentrations of the auxiliary electrolytes in dichloromethane as compared to those found in more polar acetonitrile (and propylene carbonate) and by the calculated interaction energies of such complexes in various solvents. The decrease in the magnitude of the interaction energies with the increase in solvent polarity was related primarily to the difference between solvation energy of the free anion and anion−$\pi$ complex (due to higher effective ionic radii of the latter), which can be well-explained by the Born model. The addition of the auxiliary electrolyte led to the decrease in the concentration (and effective formation constants) of the complexes of the $\pi$-acceptors with halides. Due to the sharper fall of $K_{eff}$ with $I$ in dichloromethane, the values of formation constants measured at high ($I$ = 0.5) ionic strength in this relatively low-polar solvent were lower than those in more polar acetonitrile or propylene carbonate. The effects of an ionic atmosphere were related to the competing formation of the complexes of the $\pi$-acceptors with anions from the auxiliary electrolytes and to variations of activities of halides and anion−$\pi$ complexes with ionic strength (which were modeled using Debye−Hückel theory). Such interplay between the effects of solvent polarity and ionic atmosphere should be taken into account when comparing experimental data with results of the calculations and in the design of the systems for molecular recognition and catalysis. Importantly, while the formation of the complexes of $\pi$-acceptors with halides is accompanied by appearance of new (change transfer) absorption bands, the UV−Vis spectra of complexes with non-halide anions were very close to the spectra of the individual components. These differences suggest that although charge−transfer interaction apparently plays a critical role in formation of the formers, it is probably negligible in the complexes of the latter.


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It should be also noted that the variations in the absorption intensities of the complexes with the concentration of the anions can be well-modeled using 1:1 isotherms (or the Benesi−Hildebrand equation), regardless of if they were measured under conditions of constant and variable ionic strengths. The effective formation constants obtained in the presence of the auxiliary electrolyte ($I$ = const) were lower than those measured without addition of $Bu_4NPF_6$ (variable ionic strength). However, the values measured in the presence of any supporting electrolyte should be determined with the explicit consideration of the competing complexes. Once associations with $PF_6^-$ were taken into account, the formation constants of the complexes of $\pi$-acceptors with halides measured under conditions of constant and variable ionic strength in acetonitrile were within the accuracy limits. This confirms the validity of the reported literature values of the formation constants measured in the polar solvents under conditions of variable ionic strength.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.2c03491.

> Additional experimental details including UV−Vis spectral data for titration of $\pi$-acceptors with halide anions and effects of auxiliary electrolytes on the UV−Vis spectra of $\pi$-acceptors, details of calculations of formation constants and theoretical computations of interaction energies, and results of QTAIM analyses of the anion−$\pi$ complexes (PDF)

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### Notes

The authors declare no competing financial interest.

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