Concentration-Dependent Isotope Effects in Electron Transfer-Mediated Reactions Photocyanation of Biphenyl and Dimethylbiphenyls

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The magnitude of the hydrogen−deuterium isotope effect (IE) in the photosensitized cyanation of biphenyl is found to depend on the concentration of biphenyl and on that of cyanide, as well as on the ionic strength of the medium. These concentration dependences are shown to originate from intermolecular electron exchange between biphenyl and its radical cation, in competition with addition of cyanide. Similar observations are made for the three symmetrically substituted dimethylbiphenyls upon deuteration of the methyl groups. The overall magnitude of the IE is determined by the IE of the back electron transfer step within the initially formed ion pair, as well as by the IE of the electron exchange equilibration. The experimentally determined equilibrium IEs for the biphenyls are in agreement with the results of semiempirical and ab initio calculations.

Introduction

In the past decades, radical cations have been recognized as important intermediates in biological systems[1] as well as in organic synthesis.[2] This has triggered numerous investigations of the physical properties and chemical reactivity of a wide range of organic radical cations, using (time-resolved) optical,[3] electrochemical,[4] chemical,[5] and theoretical methods.[3,6]

Isotope effects (IEs) have proven to be a useful tool to gain insight into reaction mechanisms.[7] The most convenient way to measure IEs is by performing competition experiments with the substrate and its isotopomer or isotopologue in one reaction vessel. With this intraexperimental method, the reaction conditions are by definition the same for the two isotopically substituted substrates.

In our laboratories, it has been shown that in the analysis of such intraexperimentally determined IEs transfer of "reactivity" has to be taken into account.[8,9] For instance, in the photocyanation of naphthalene, the dependence of the magnitude of the IE on the naphthalene concentration is the consequence of exchange of an exciton between a singlet excited and a ground state naphthalene molecule (eq 1).[9] The IE increases from ∼1 at low naphthalene concentrations to 1.35 at high concentrations. The equilibrium constant $K > 1$ leads to preponderance of the $C_{10}H_8$ singlet excited state and to preferential reaction of the hydrogenated compound and thus to a normal IE (>1).

$$C_{10}H_8 + C_{10}D_8{}^{S_1} \overset{K > 1.4}{\rightleftharpoons} C_{10}D_8 + C_{10}H_8{}^{S_1} \qquad (1)$$

Concentration-dependent IEs may also occur in reactions in which intermediates exchange an electron before reacting to product. A molecule M_H can donate an electron to the radical cation of its isotopologue M_D, yielding neutral M_D and the radical cation of M_H (eq 2). For such a reaction step to contribute to the overall IE, its equilibrium constant (K) has to differ significantly from 1. This can indeed be expected to be the case; for instance, the effect of deuterium substitution on the electron exchange has been studied for thianthrene, and its K was determined to be 0.62.[10]

$$M_H + M_D{}^{+\bullet} \overset{K}{\rightleftharpoons} M_D + M_H{}^{+\bullet} \qquad (2)$$

In this study, the implications of electron exchange between neutral and radical cation isotopologues on the overall IE of a nucleophilic aromatic photosubstitution involving such species were investigated by varying the substrate and nucleophile concentrations. Biphenyl (BP) was chosen as the model substrate for several reasons: (i) Its radical cation ($BP^{+\bullet}$) can be easily photogenerated by selective excitation of 1,4-dicyanonaphthalene (DCN) in the presence of BP.[11] In this way, exciton exchange as depicted in eq 1 cannot occur. (ii) Although initially ion pairs (IPs) are formed, the quantum yield of separated $BP^{+\bullet}$ is high.[12,13] Substantial separation of the ions is required, because otherwise the radical ion reacts with its counterion (i.e., back electron transfer (ET)) or with a nucleophile within the solvent cage preventing the electron exchange of eq 2. (iii) $BP^{+\bullet}$ readily reacts with cyanide, yielding photocyanation products (eq 3).[14,15] This allows determination of the IE on the product formation. (iv) Understanding the kinetics of ET to $BP^{+\bullet}$ is desirable, because BP is a versatile cosensitizer for the generation of otherwise inaccessible radical cations.[16]

In addition to the effect of replacement of the hydrogen atoms in BP by deuterium, the effect of deuteration of methyl substituents at aromatic ring positions in three dimethylbiphenyls (DMBPs) has also been investigated. Generation of the radical cations of DMBPs under photoinduced ET conditions by use of appropriate electron acceptors also gives high quantum yields of separated ions and thus also allows determination of the IEs on the electron exchange equilibria.[12] The three symmetrically substituted DMBPs were chosen to reduce the number of nonequivalent cyanation positions.

Experimental Section

Materials. BP and BP-d_{10} were both purified by repeated crystallization from acetonitrile. 3,3′-DMBP was purified by Kugelrohr distillation, and 4,4′-DMBP was used as received. All compounds were obtained from Aldrich. The acetonitrile

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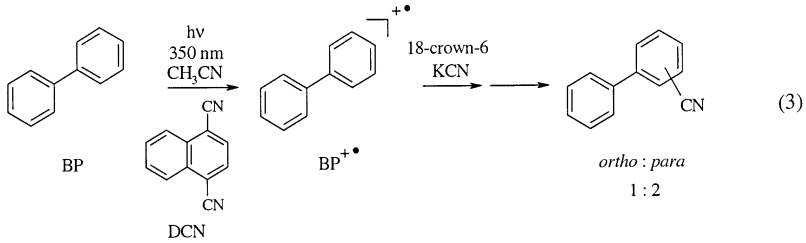
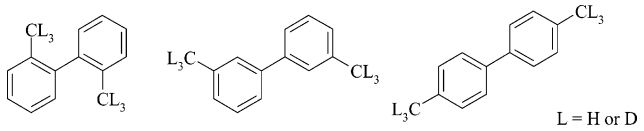


(3)

(high-performance liquid chromatography (HPLC) grade; Rathburn) for the irradiations was used as received. All materials for the syntheses (Acros or Aldrich) were used as received. The 18-crown-6/KCN complex ($^{18}C^6$-KCN) was prepared according to a literature procedure.[17] The same procedure was used to make the 18-crown-6/KPF_6 complex ($^{18}C^6$-KPF_6).



2,2'-DMBP 3,3'-DMBP 4,4'-DMBP

The ET sensitizer DCN was prepared from 1,4-dibromonaphthalene[18] according to method C described in ref 19. The product was purified by crystallization from acetonitrile and sublimation, after which the sample was still contaminated with ~5% 1,5-dicyanonaphthalene. Further purification of the mixture was not attempted, since it gave efficient photocyanation. ^{1}H NMR: δ (ppm) 7.9 (q, 2.5H), 8.0 (s, 2H), 8.4 (q, 2.5H). MS *m*/*z* (rel. int.): 178 (100), 151 (22), 124 (8).

2,2′-DMBP was prepared from 2,2′-diformylbiphenyl[20] by a Wolff−Kishner reduction: 10 g of 2,2′-diformylbiphenyl and 25 mL of hydrazine monohydrate were stirred in 300 mL of ethylene glycol for 1 h. To the mixture, 25 g of KOH was added, and it was refluxed for 2 h, after which it was cooled to room temperature and 100 mL of water was added. Subsequently, the mixture was extracted with 300 mL of diethyl ether and the organic layer was washed with water and dried on $MgSO_4$. After the solvent was removed under reduced pressure, the crude product was purified by column chromatography on silica gel (eluent: pet. ether (40/60):diethyl ether = 20:1) and Kugelrohr distillation. ^{1}H NMR: δ (ppm) 2.1 (s, 6H), 7.0−7.3 (m, 8H). MS *m*/*z* (rel. int.): 182 (100), 167 (38).

For the deuteration of 4,4′-DMBP, 330 mg (13.8 mmol) of dry sodium hydride (95%) was suspended in 5 mL of dimethyl sulfoxide-d_6. This was stirred for 15 min after which 2.5 g (13.7 mmol) of 4,4′-DMBP was added and the mixture was stirred overnight at 75 °C. The mixture was cooled to room temperature, ~5 mL of D_2O was added, and stirring was continued for 15 min. The suspension was extracted with diethyl ether, and the organic layer was dried on $MgSO_4$ and concentrated. This procedure was repeated twice. After the final exchange step, the crude product was purified by column chromatography on silica gel (eluents: pet. ether (40/60):diethyl ether = 15:1). ^{1}H NMR: δ (ppm) 7.0 (d, 4H), 7.24 (d, 4H) (100% methyl deuteration according to NMR). MS *m*/*z* (rel. int.): 188 (100), 170 (40).

3,3′-DMBP and 2,2′-DMBP were deuterated by the same procedure as described above and were purified by Kugelrohr distillation. 3,3′-DMBP-d_6: ^{1}H NMR: δ (ppm) 2.3 (s, 0.3H), 7.0−7.4 (m, 8H) (96% methyl deuteration according to NMR). MS *m*/*z* (rel. int.): 188 (100), 170 (43). 2,2′-DMBP-d_6: ^{1}H NMR: δ (ppm) 2.0 (s, 0.2H), 7.0−7.4 (m, 8H) (98% methyl deuteration according to NMR). MS *m*/*z* (rel. int.): 188 (100), 170 (97).

For reference and gas−liquid chromatography reponse calibration purposes, 4-cyanobiphenyl was prepared from 4-bromobiphenyl[21] by the same cyanation method as used above in the preparation of DCN. ^{1}H NMR: δ (ppm) 7.4−7.7 (m). MS *m*/*z* (rel. int.): 179 (100), 152 (11). 4-Cyanobiphenyl-d_9 was prepared accordingly from 4-bromobiphenyl-d_9.

A mixture of 2- and 3-cyano-4,4′-DMBP was prepared from a mixture of 2- and 3-bromo-4,4′-DMBP[22] by the same cyanation method as used above in the preparation of DCN. A mixture of 2- and 3-cyano-4,4′-DMBP-d_9 was prepared accordingly. ^{1}H NMR: δ (ppm) 2.4 (s, 5.5H), 2.6 (s, 0.4H), 7.1−7.6 (m, 7H) (7% 3-cyanobiphenyl).

Irradiations. Air-saturated solutions of 2.0 mM DCN and varying concentrations of $^{18}C^6$-KCN, $^{18}C^6$-KPF_6, and BP-h_{10}/BP-d_{10} (the latter two always present in ~1:1 ratio) in acetonitrile were prepared. They were illuminated in 10 mL Pyrex tubes in a Rayonet Photochemical Reactor RPR 200 fitted with seven 350 nm lamps, which was placed in a cool room (4 °C). The temperature of all reaction mixtures remained constant at 12 °C during the irradiations, and for all kinetic measurements, samples were brought to this temperature prior to irradiation. At appropriate time intervals (up to the desired conversion, 5−15%, depending on ionic strength and cyanide and BP concentrations), ~1 mL aliquots were taken from the solution and injected in a test tube containing ~1 mL of water and ~1 mL of diethyl ether. The layers were agitated vigorously, and the organic layer was removed with a pipet, after which it was analyzed on analytical GC and/or GC-MS. In the case of BP, the IEs are determined on the formation of *o*-cyanobiphenyl, because a minor impurity caused a larger statistical error when the IEs were determined on the *p*-isomer. In the case of the DMBPs, the IEs are determined on the formation of the major product. In all cases, the trends in the variation of the IE were, however, the same for all isomers of the cyanation products.

Fluorescence. The fluorescence spectra for the Stern−Volmer plots were measured at λ_{exc} = 315 nm. Air-saturated stock solutions of DCN (2.3 mM) and BP (100 mM) in acetonitrile were mixed and diluted to make samples of constant DCN concentration (~23 μM) and varying BP concentrations (0−80 mM).

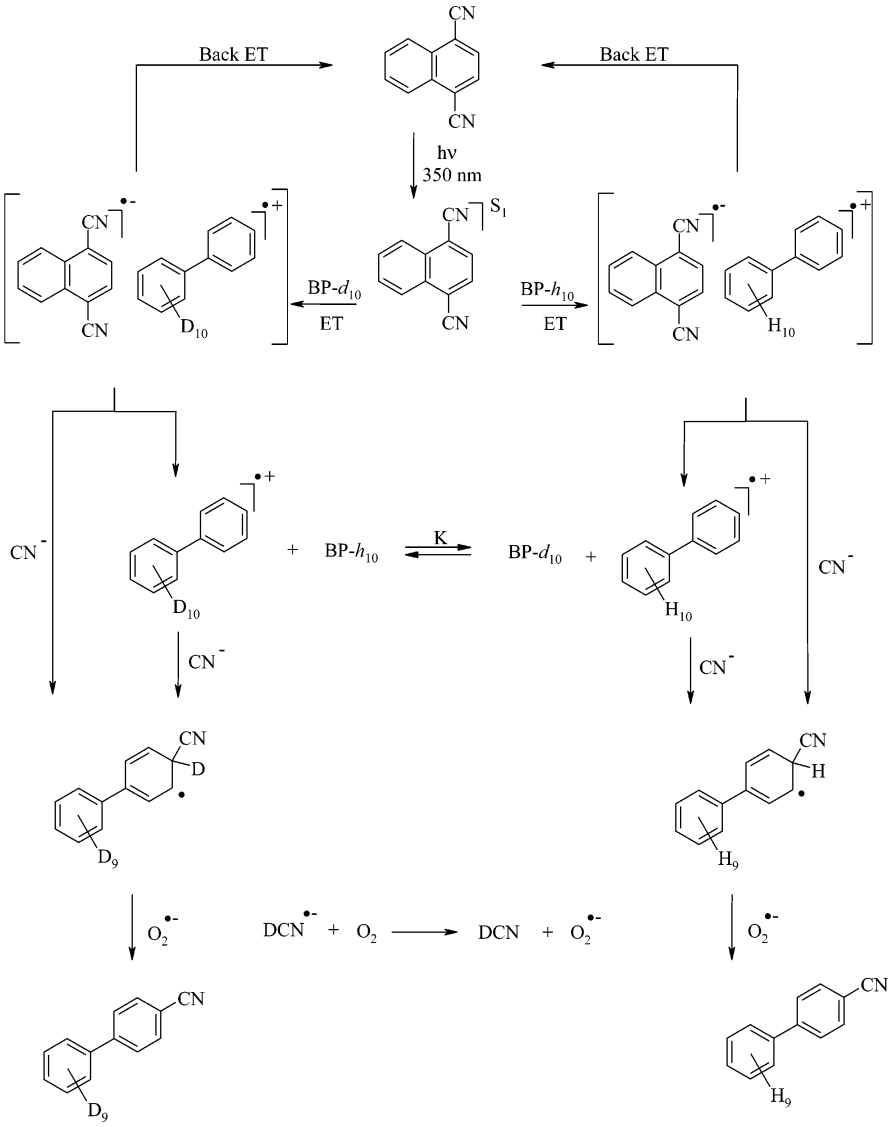
Time-Resolved Experiments. The setup used to measure the IE on the formation of free BP radical cations ($BP^{+\bullet}$) has been described in ref 23. The relative amount of free BP-$h_{10}^{+\bullet}$ and BP-$d_{10}^{+\bullet}$ formed immediately after the laser pulse was determined from a fit of decay of $BP^{+\bullet}$ for both isotopologues to

$$[BP^{+\bullet}]_t = \frac{[BP^{+\bullet}]_0}{1 + kt[BP^{+\bullet}]_0}$$

where k is the decay rate of $BP^{+\bullet}$.[24] The IE on the efficiency of formation of free $BP^{+\bullet}$ is determined as the quotient of $[BP^{+\bullet}]_0$ for BP-h_{10} and -d_{10}.

Equipment. The 200 MHz NMR spectra were recorded on a JEOL JNM FX-200 spectrometer, and the 300 MHz NMR spectra were recorded on a Bruker WM300 spectrometer. GC

SCHEME 1: Postulated Mechanism for the Photocyanation of a BP-h_{10}/BP-d_{10} Mixture via ET (Only the *para* Mode of Attack of CN^- at $BP^{+\bullet}$ Is Depicted)



analyses of the reaction mixtures were performed with a Hewlett-Packard 6890 series GC equipped with a WCOT fused silica CP-SIL-5CB (25 m) column and a flame ionization detector (FID). With this technique, the isotopologues of the reactants as well as the reaction products were almost baseline separated. The FID was calibrated, using synthesized or commercially available (isotopologues) materials. Isomers were assumed to have equal response factors. An HP Chemstation was used for analysis of the analytical GC data. All GC-MS spectra were recorded on a Packard model 438A GC equipped with a CP-SIL-5CB (25 m) column, coupled with a Finnigan ITD 700 mass spectrometer. Fluorescence spectra were recorded on a SPEX Fluorolog II equipped with a SPEX Torin TA300 photomultiplier.

Calculations. Semiempirical RHF and ROHF calculations on the BPs and BP radical cations, respectively, using the PM3 parametrization set as implemented in MOPAC 93,[25] were performed on an IBM RS/6000 platform. After preoptimization, the final structures were obtained by optimization with the eigenvector following method. With the thus obtained geometries, frequency calculations were performed, and the effect of isotopic substitution on the zero point energies (ZPEs) was determined.

Ab initio calculations were performed using the GAUSSIAN 98 (revision A5)[26] set of programs on the same computer. The calculations of the neutral BPs were performed on the B3LYP/6-31G(d,p) level of theory. For the radical cations, the corresponding unrestricted method was employed. Charge distributions were calculated using the NBO 3.1 program,[27] and for all reported charges, the hydrogens are summed into the heavy atoms. All charges on carbon atoms are reported as the sum of the charge on the carbon atom and the charges on the hydrogen atoms connected to it.

Results and Discussion

Mechanism. The mechanism of photocyanation of unsubstituted aromatic compounds, such as BP, in the presence of electron acceptors is of the $S_{R+N}Ar$ type.[14,17,28] Singlet excited DCN acquires an electron from BP to yield an IP.[11] Back ET within the IP yields the ground states of DCN and BP, and separation of the IP gives two free radical ions.[12,13] Cyanide attack can occur both at the aromatic radical cation within the IP and at the free radical cation, to yield the cyanohydrogen radical.[9] Prior to cyanation, the free radical cation may also give electron exchange with a neutral substrate molecule.[10] The cyanohydrogen radical species rapidly reacts with the radical

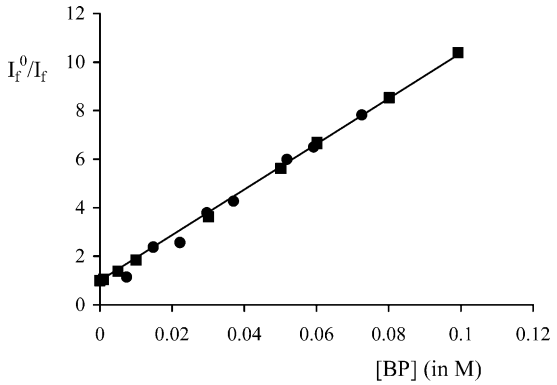


Figure 1. Stern−Volmer plots of the quenching of the fluorescence of DCN by BP-h_{10} (■) and BP-d_{10} (●) in acetonitrile.

anion of oxygen by hydrogen atom transfer, yielding the cyanoaromatic. DCN is regenerated from the radical anion of the electron acceptor by reaction with oxygen.[9] On the basis of the results of these studies, the detailed mechanism of Scheme 1 is postulated for the photocyanation of BP, and all of the IEs will be discussed in the framework thereof.

On the basis of Scheme 1, IEs upon BP deuteration may stem from three reaction steps: (I) ET from BP to the excited DCN, (II) back ET from the DCN radical anion to the $BP^{+\bullet}$ within the IP, and (III) electron exchange between neutral BP and its radical cation. No substantial IE is expected on the addition of the cyanide anion, since this step is (nearly) diffusion controlled,[9,29,30] or on the hydrogen atom abstraction step by the oxygen radical anion, since this is not a rate-determining step in aerated solutions.[9]

The importance of step I for the overall IE will be investigated by measuring the IE on the Stern−Volmer quenching constant. The importance of steps II and III will be clarified by the study of the effect of the cyanide and BP concentration on the magnitude of the IE.

Fluorescence Quenching. BP efficiently quenches the fluorescence of DCN by an ET mechanism.[11] To study whether there is an IE on this ET step, the Stern−Volmer constants for quenching of singlet excited DCN with BP-h_{10} and BP-d_{10} were measured in acetonitrile. In both cases, linear plots were obtained (Figure 1) and the Stern−Volmer constants for BP-h_{10} (k_{SV} = 93.8 (±0.6) M^{-1}) and BP-d_{10} (k_{SV} = 91.9 (±2.4) M^{-1}) are identical within experimental error (IE = 1.02 ± 0.03). In oxygen-free samples, a value of k_{SV} of 141 M^{-1} has been measured.[11] The presence of oxygen in our samples reduces the lifetime of the singlet excited state of DCN. This accounts for the lower Stern−Volmer constant, since $k_{SV} = k_q \times \tau_S$ where k_q is the rate of quenching by DCN and τ_S is the DCN singlet lifetime. Competitive quenching of the DCN fluorescence by oxygen and BP thus lowers the Stern−Volmer constants.

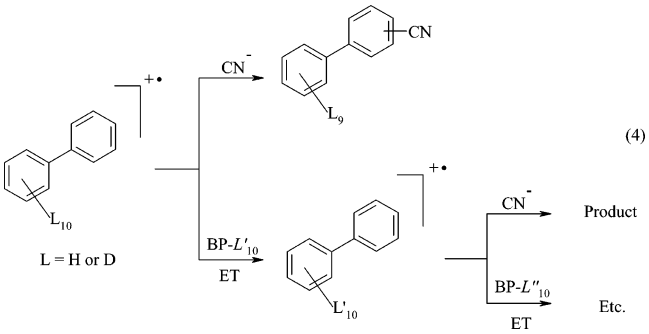
The ET step from BP to singlet excited DCN thus is not affected by deuteration of BP. The IE being close (or equal) to unity can simply be understood. The rate of quenching of DCN by BP-h_{10} has previously been found to be diffusion controlled,[11] and deuterium substitution will hardly affect the rate of diffusion. Because the IE on the quenching step equals one within experimental error, this step (step I) will therefore not play a role in the overall IE on the photocyanation of BP. An IE will therefore exclusively be caused by steps II and/or III.

Concentration-Dependent IEs. The photocyanation of mixtures of BP-h_{10} and BP-d_{10} was achieved using 18-crown-6-KCN as the cyanide donor to free the cyanide nucleophile from its counterion.[9,17] In the study of the intraexperimental IEs on the photocyanation of naphthalene, the ratio of cyanation at the 1- and 2-positions of naphthalene was observed to vary with the cyanide concentration.[9] This is ascribed to attack by cyanide at the IP at high cyanide concentrations and at the free naphthalene radical cation at low cyanide concentrations. The geminate radical IP is somewhat more selective for reaction with cyanide ion than the free radical ion. In the DCN-sensitized photocyanation of BP, the ratio of ortho to para substitution does not vary within experimental error, upon changing the cyanide concentration. The difference is due to the high efficiency of ion separation in the case of BP (cf. Scheme 1).[12,13] Almost all of the product is formed by cyanide attack at free $BP^{+\bullet}$.

The IEs on this reaction as a function of both the cyanide and the BP concentration, at constant ionic strength (I = ∼50 mM; maintained constant using 18-crown-6-KPF_6) are depicted in Figure 2 (the collected data are given in Table 1 of the Supporting Information).[31]

The IEs are seen to vary from 0.94 to 1.10 as a function of the concentrations of both reactants. Three general trends emerge from Figure 2: (i) The IE decreases from normal to inverse with increasing BP concentration. (ii) The IE increases from inverse to normal with increasing cyanide concentration. (iii) At low BP concentrations, the variation of the IE with the cyanide concentration (almost) disappears. The same is true for the variation of the IE with the BP concentration at high cyanide concentrations.

All observations are in agreement with the mechanism presented in Scheme 1 including electron exchange and a value of the equilibrium constant for the electron exchange step K < 1. The IEs are caused by the competition of cyanide and neutral BP in their reaction with $BP^{+\bullet}$ (eq 4). In the first case, substitution by cyanide occurs and in the latter electron exchange.



(4)

(i) The variation of the IE with the BP concentration is the result of the occurrence of the electron exchange step. The cyanation at very low BP concentrations has a small normal IE (vide infra). In that case, the electron exchange between neutral BP at $BP^{+\bullet}$ cannot compete with attack of negatively charged cyanide at $BP^{+\bullet}$. Upon increasing the concentration of BP, equilibration by electron exchange becomes important and competes with the reaction of $BP^{+\bullet}$ with cyanide. With K < 1, increasing the BP concentration decreases the relative amount of BP-$h_{10}{}^{+\bullet}$ and the IE becomes smaller.

(ii) The increase of the IE with increasing cyanide concentration is also caused by the electron exchange. At higher cyanide concentrations, reaction of $BP^{+\bullet}$ with cyanide occurs more efficiently than equilibration by electron exchange. The extent of equilibration thus depends on the cyanide concentration. With K < 1, upon increasing the cyanide concentration, electron exchange equilibration becomes less important and the IE becomes larger.

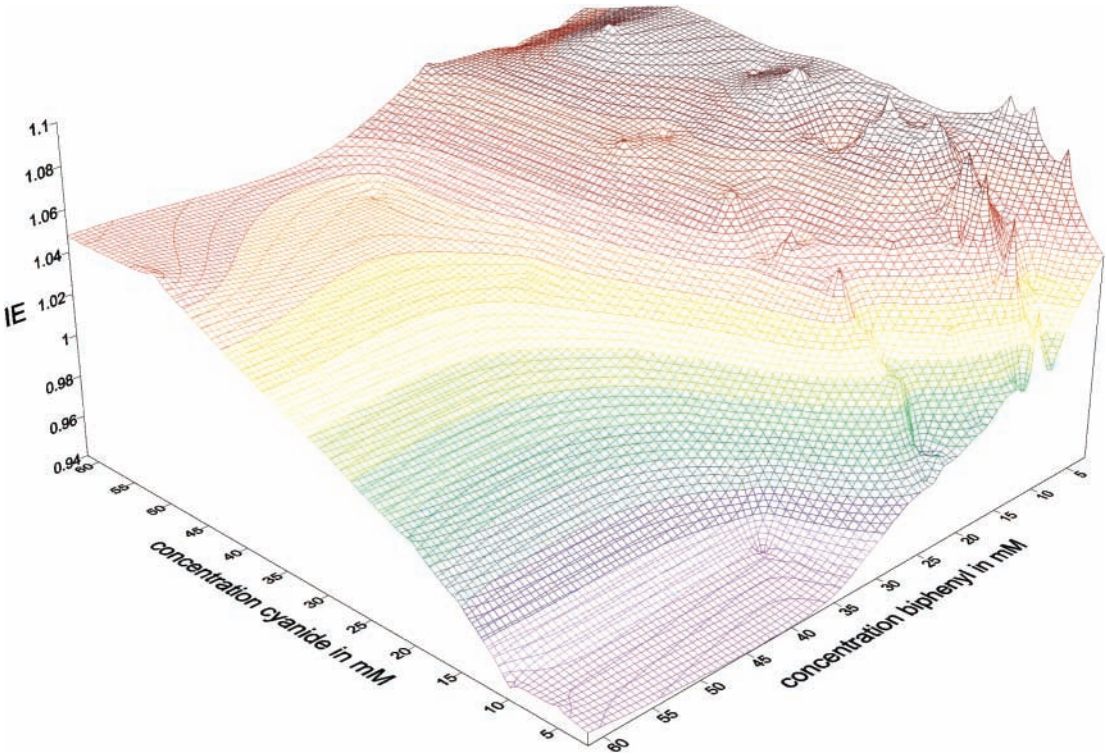
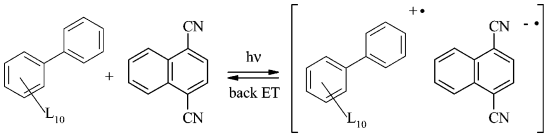


Figure 2. Intraexperimental IEs on the photocyanation of BP as a function of the cyanide and the BP concentration.

(iii) At very low BP concentrations, equilibration by the electron exchange mechanism does not (or hardly) occur, because this reaction between a charged and a neutral species is far slower than the cyanide addition, which is a reaction between two oppositely charged particles. In that situation, the cyanide concentration thus has no (or little) effect on the IE. Similarly, at very high cyanide concentrations, the reaction of $BP^{+\bullet}$ with cyanide (cation−anion reaction) is too fast for the electron exchange (cation−molecule reaction) to compete and the BP concentration has no (or little) effect on the IE.

The equilibrium constant K (i.e., the equilibrium IE) for the electron exchange step can be estimated to be ∼0.9 on the basis of the asymptotic value to which the IE levels off. Such an inverse IE is in line with the previously reported electron exchange equilibrium for thianthrene-h_8/-d_8 and its radical cation (equilibrium IE = 0.62)[10] and with computations (vide infra). Deuterium substitution has been found to reduce the electron affinity of both positively charged and neutral aromatic substrates.[10,32] The reduced electron affinity of deuterium-substituted isotopologues is due to the larger electron-donating effect of deuterium ($\sigma_{I,F} = -0.0011$) as compared to hydrogen.[33]

The IE at very low BP concentrations is significantly larger than 1 (∼1.10). This is unexpected since the Stern−Volmer quenching experiments show that the hydrogenated and deuterated radical cations of BP are formed with equal efficiency. Thus, the deviation from 1 cannot be due to an IE on the formation of $BP^{+\bullet}$. Furthermore, at these very low BP concentrations, equilibration by electron exchange cannot occur (vide supra). Therefore, the only reaction step that can account for this IE is back ET within the IP, leading to neutral ground state BP and DCN (eq 5). The back ET step within an IP is usually exothermic and thus lies in the "Marcus inverted region", so the rate of the ET decreases with increasing driving force. Because the BP-d_{10} radical cation is more stable than the BP-h_{10} radical cation (vide supra), back ET will be less exothermic and thus faster for BP-d_{10} than for BP-h_{10}. In agreement with this, the IEs on the back ET step for benzene and *p*-xylene have been reported to be inverse.[34] An inverse IE means that relatively more of the BP-h_{10} than the BP-d_{10} radical cation is formed, resulting in a normal IE on the cyanation reaction in the absence of electron exchange equilibration, as observed!



(5)

L = H or D

The IE on the formation of free $BP^{+\bullet}$ from BP and DCN was independently measured using transient absorption spectroscopy. This method has previously been used to determine the IE on back ET reactions.[35,36] The amount of free $BP^{+\bullet}$ that is formed immediately after the laser pulse is measured for hydrogenated and deuterated BP. This method gives an IE on the formation of free $BP^{+\bullet}$ of 1.06 ± 0.02. In the absence of cyanide, the two competing pathways for the IP are the back ET and separation of the ions. Because the IE on separation (i.e., formation of free $BP^{+\bullet}$) is normal, the IE on the back ET must be inverse, as predicted from the IEs on the photocyanation. The magnitude of the IE also is in excellent agreement with our photocyanation result of ∼1.10. Thus, the IE on the photocyanation at low BP concentrations and at high cyanide concentrations is governed by the back ET step.

Salt Effect. The ionic strength of a solution has a significant effect on the lifetime of radical ions.[37] Because the lifetime of $BP^{+\bullet}$ plays a crucial role in its availability for electron exchange equilibration prior to cyanation (eq 4), ionic strength is expected to affect the IE. In Figure 3, the IE is given as a function of the ionic strength I, increased by addition of 18-crown-6/KPF_6, while keeping the BP and cyanide concentrations constant.

The variation of the IE of cyanation of BP with the ionic strength provides further evidence for the radical cation equilibration causing the concentration-dependent IE. For

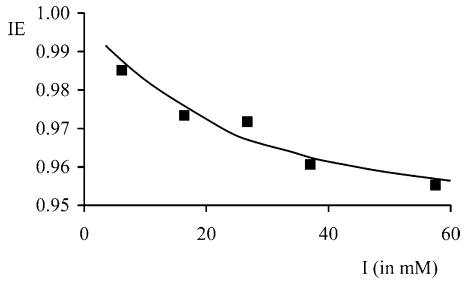


Figure 3. Dependence of the IE on the photocyanation of BP on the ionic strength, varied by addition of 18-crown-6/KPF_6, at constant BP (22.9 mM) and cyanide (6.2 mM) concentrations.

instance, when equilibration occurs by singlet exciton exchange (eq 1), there is no effect of the ionic strength on the IE, since in that case no charged species is involved in the equilibration step.[9]

In the present case, the decrease of the IE with increasing ionic strength is due to the increase in stability of $BP^{+\bullet}$. At higher ionic strengths (more inert $^{18}C^6$-KPF_6 salt added), the lifetime of radical cations is higher, because the positively charged ions are shielded from the negatively charged cyanide ions by the hexafluorophosphate ions.[38] Their shielding results in a significant reduction of the efficiency of the photocyanation reaction. Because the electron exchange reaction that causes the concentration dependence of the IE does not involve an ion−ion reaction, it is less affected by the addition of an inert salt. The relative larger importance of the ET step (with $K < 1$) at higher salt concentrations leads to a lower IE.

At higher salt concentrations, $BP^{+\bullet}$ thus is less reactive and more selective. This conclusion has practical value to widen the scope of the BP/DCN donor/acceptor system for the photochemical generation of radical cations, which are inaccessible by direct irradiation of a donor.[16] In the presence of more than one electron donor, the selectivity of their formation can be altered by changing the ionic strength of the solution, especially for differently charged electron donors.

Methyl-Substituted BPs. The inverse equilibrium IE on the electron exchange between BP and $BP^{+\bullet}$ is due to the inductive electron-releasing effect of the ring deuterium atoms (vide supra). In the case of deuteration of the methyl group of methylated BPs, a normal equilibrium IE is expected on the basis of the larger hyperconjugative stabilization of the cationic charge by methyl hydrogen atoms than by methyl deuterium atoms. This effect is much larger than the inductive effect.[39] This means that now upon increasing the concentration of the substrate the IE is expected to increase. The magnitude of the hyperconjugative effect and thus of the equilibrium IEs of methyl-substituted BPs will depend on the charge on the adjacent (aromatic) carbon atom and can therefore give information about the charge distribution in the radical cations. The influence of ortho methyl substituents in BP is of special interest. In neutral BP, the planes of the two aromatic rings are at a ∼40° angle according to experiment[40] and calculations,[41] but in the case of $BP^{+\bullet}$, experiments[42] as well as computations[41b] indicate a more planar structure (0−20°). Methyl substituents at the ortho positions prevent planarity and thus the conjugation of the two phenyl rings. This may affect the charge distribution in the radical cation and therefore also the equilibrium IE.

IEs on back ET within an IP are also very different upon deuteration of a methyl substituent instead of the aromatic ring. For several methyl-substituted benzenes, normal IEs on the back ET step are reported.[35,36]

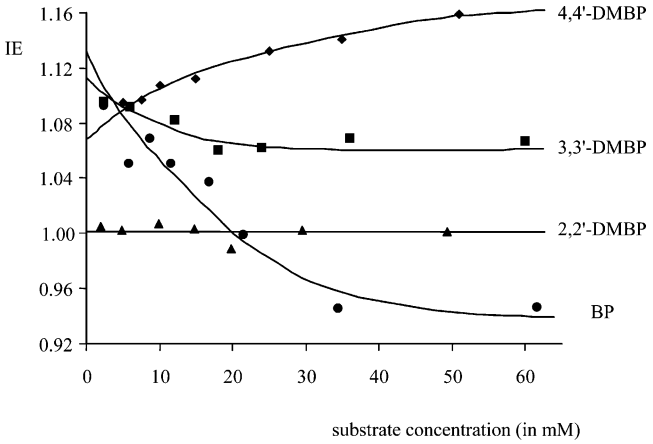


Figure 4. IEs of the photocyanation of 2,2′-DMBP (▲), 3,3′-DMBP (■), and 4,4′-DMBP (◆) as a function of the DMBP concentration at constant ionic strength ($I = \sim$50 mM) and cyanide concentration (∼10 mM).

Upon irradiation of DCN in the presence of the DMBPs, in principle, four different monoring cyanation products can be formed from both 2,2′- and 3,3′-DMBP and two from 4,4′-DMBP. Both 2,2′- and 3,3′-DMBP do yield three monoring cyanation products (in a ratio of 1:1.5:23.0 and 1:1.1:3.9, respectively), and 4,4′-DMBP yields two monocyanation products (in a 1:8.7 ratio). The position of ring cyanation in the products was not determined. Cyanation of the methyl groups does not occur. The IEs were measured using the product formed in the largest amount for each compound. The IEs on the formation of that photocyanation product as a function of the DMBP concentration are given in Figure 4 (the collected data are given in Table 2 of the Supporting Information). The corresponding data for BP are added for comparison.

Clearly, the trends in the variation of the IEs with the concentrations of the substrates are influenced by the presence of methyl groups. Within experimental error, the IE on the photocyanation of 2,2′-DMBP equals 1 throughout the explored concentration range. The IE on the photocyanation of 3,3′-DMBP slightly decreases with increasing DMBP concentration and that of 4,4′-DMBP increases. At very low DMBP concentrations, the IE for both compounds is ∼1.1. The IEs for 3,3′- and 4,4′-DMBP level off to ∼1.05 and ∼1.15, respectively.

These trends can also be rationalized using the mechanism of photocyanation as proposed for BP (see Scheme 1) but now with an equilibrium constant $K > 1$ for the electron exchange process (see eq 2). The 3,3′- and 4,4′-DMBP exhibit normal equilibrium IEs on the electron exchange step, since they both level off to a value higher than 1 at high concentrations. The normal equilibrium IEs are caused by hyperconjugative stabilization of the positive charge on the aromatic ring by the methyl groups. This stabilization is reduced upon deuteration, resulting in preferential formation of hydrogenated $DMBP^{+\bullet}$.

The magnitudes of the (inverse) IEs on the back ET step are similar for 3,3′- and 4,4′-DMBP, as reflected in their equal normal IE (∼1.1) at low DMBP concentrations. This is remarkable, because xylenes show normal IEs for back ET upon methyl deuteration,[35] so an inverse IE for cyanation at low concentrations was expected. The reason for this dichotomy is not clear.

Although the IEs for 3,3′- and 4,4′-DMBP are similar at low DMBP concentrations, they deviate significantly at higher concentrations. The IE for 3,3′-DMBP becomes smaller with increasing DMBP concentration, because the electron exchange equilibrium IE is smaller than the IE on the formation of the

TABLE 1: PM3 and B3LYP/6-31G(d,p) Calculated ZPE Differences (in cal/mol) for the Electron Exchange Equilibria of Eq 6 and the Equilibrium IE (K) at 285 K[a]

	PM3		B3LYP/6-31G(d,p)		experiment
	ΔZPE	IE	ΔZPE	IE	IE
BP	+65	0.89	+117	0.81	0.9
2,2′-DMBP	+134	0.79	+19	0.97	1.00
3,3′-DMBP	−46	1.08	+58	0.90	1.05
4,4′-DMBP	−129	1.26	−39	1.07	1.2

[a] The (estimated) experimental values are added for comparison.

free DMBP$^{+\bullet}$. Similarly, the IE for 4,4′-DMBP becomes larger with increasing DMBP concentration, because the electron exchange equilibrium IE is larger.

Taking the IE upon deuteration of the methyl groups as a measure of the charge distribution within the radical cations of the BPs, the positions in order of diminishing charge are 4 > 3. This is in agreement with the results of semiempirical and ab initio calculations of the magnitudes of the equilibrium IEs and of the changes in the atomic charges, as shown in the next section.

For 2,2′-DMBP, one may conclude that apparently there is no IE on either the back ET step or the electron exchange equilibrium. The first possibility accounts for a unity IE at low DMBP concentrations and the second for a unity IE at high concentrations. However, an equilibrium IE of one is unlikely, because a significant charge increase is calculated at the 2- and 2′-positions in 2,2′-DMBP upon ionization (vide infra). Alternatively, the equilibrium IE may be significant but is not expressed because the electron exchange is slow. In that case, equilibration cannot compete with cyanation. The inability of 2,2′-DMBP$^{+\bullet}$ to acquire a (near) planar geometry causes the charge to be mainly localized on one of the two phenyl rings. The molecule behaves more as a monosubstituted benzene than as a BP in the electron exchange. This may slow the exchange. A third possibility is that because 2,2′-DMBP$^{+\bullet}$ is not planar (and thus less stable than BP$^{+\bullet}$ and the two other DMBPs$^{+\bullet}$) the cyanation occurs before dissociation of the IP occurs. As argued before, the dissociation is crucial for the electron exchange equilibration. The results presented here do not allow a choice between the explanations.

Calculations. Semiempirical[32c,43] and ab initio[44] molecular orbital calculations have proven to be useful in the evaluation of electron exchange equilibrium IEs. Generally, however, the origin of an equilibrium IE is complex, since the total change in ZPE stems from a number of opposing IEs on the various vibrations.[43a]

$$C_{12}H_{10} + C_{12}D_{10}^{+\bullet} \overset{K}{\rightleftharpoons} C_{12}D_{10} + C_{12}H_{10}^{+\bullet}$$

$$C_{14}H_{14} + C_{14}H_8D_6^{+\bullet} \overset{K}{\rightleftharpoons} C_{14}H_8D_6 + C_{14}H_{14}^{+\bullet} \qquad (6)$$

In Table 1, the changes in ZPEs for the electron exchange equilibria depicted in eq 6 are given. From these, the equilibrium IEs at 285 K, the temperature at which the experiments were performed, are calculated.

The PM3 calculations give good predictions of the directions as well as the magnitudes of the equilibrium IEs, with the exception of the IE for 2,2′-DMBP. In the PM3 calculations, all cations studied are planar except 2,2′-DMBP$^{+\bullet}$ (for this cation, the angle between the two rings is 40°). The angle between the two aromatic rings is determined by two opposing effects: (i) maximization of the conjugation of the phenylic

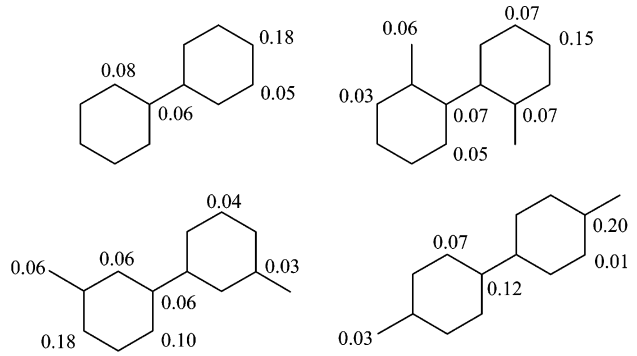


Figure 5. Changes in NBO charge density in the B3LYP/6-31G(d,p) optimized structures upon ionization of BP and the DMBPs.

π-systems, moving the two rings in a plane and (ii) steric interaction of the methyl groups with the ortho hydrogen atoms of the phenyl rings, forcing the rings out of a plane. Semiempirical calculations, such as PM3, often give a poor description of steric interactions, and this may well cause the deviation of the calculated from the experimental IE for 2,2′-DMBP.

Surprisingly, the results of the DFT ab initio calculations deviate more from the experimental values than the PM3 calculations, but in this case, the IE for 2,2′-DMBP is calculated correctly. At this level of theory, the radical cations are calculated not to be planar. The torsion angle between the two phenyl rings is ~20° for BP$^{+\bullet}$, 3,3′-, and 4,4′-DMBP$^{+\bullet}$ and 50° for 2,2′-DMBP$^{+\bullet}$. Overestimation of π-delocalization by the density functional theory method is probably the reason for the poor results for the equilibrium IEs in the higher level calculations.[45]

Calculations additionally provide the opportunity to check whether the magnitude of the equilibrium IEs in the DMBPs correlates with the changes in charge distribution upon ionization. The changes in the atomic charges calculated using the NBO method are presented in Figure 5, along with the results for the parent BP.

For all four compounds, the positive charge increase is largest at the 4-position and significantly lower at the 1-, 2- (or 6-), and 3- (or 5-) positions. The charge differences are $4 \gg 1 \approx 2 > 3$ in decreasing order. Clearly, the IEs cannot give information about the charge at the 1-position, since substitution at that carbon atom is not possible. The magnitude of the equilibrium IE of 2,2′-DMBP does not correlate with the charge increase. On the basis of the calculated charge increase, an equilibrium IE between 1.05 (that of 3,3′-DMBP) and 1.2 (that of 4,4′-DMBP) is expected. This prediction not only deviates from the experimental value but also deviates from the calculated values. The factors governing the value of the equilibrium IE of 2,2′-DMBP are thus more complex than those for the other DMBPs and are not fully understood. However, it is likely that steric interactions by the methyl groups play a dominant role. The magnitudes of the equilibrium IEs of 3,3′- and 4,4′-DMBP on the other hand do correlate with the relative charge increase at the 3- and 4-positions. The equilibrium IE is smaller for 3,3′- than for 4,4′-DMBP (1.05 and 1.2, respectively), indicating that the charge increase at the 3-position is smaller than at the 4-position, in agreement with the calculations.

Conclusions

The magnitudes of the IEs measured in the photocyanation reaction of BP initiated by excitation of DCN depend on the BP as well as on the cyanide concentration. Also, the ionic strength of the medium affects the IE. These observations can

be fully understood within a mechanism, which involves electron exchange of the BP radical cation with neutral BP. Competition of cyanide addition with electron exchange results in the observed concentration dependences. At high BP concentrations, the IE is governed by the equilibrium IE, which is inverse because of the electron-releasing character of deuterium. This is confirmed by computation of the IE with semiempirical and ab initio DFT methods. At low BP concentrations, the IE is normal, which is caused by an inverse IE on the back ET within the initially formed IP.

The concentration-dependent IEs observed upon methyl deuteration in the corresponding photocyanation reaction of 3,3′- and 4,4′-DMBP are satisfactorily interpreted within the same mechanism. Here, the equilibrium IEs are normal, due to the decreased hyperconjugative stabilization of the positive charge by the methyl group upon deuteration. This interpretation is confirmed by calculations of the change in charge distribution upon ionization. The equilibrium IE is highest in the compound that is methylated at the position of the largest charge increase (the para position).

Remarkably, no concentration-dependent IE is found for 2,2′-DMBP. This is not expected from either the calculations of the equilibrium IE or the change in charge distribution upon ionization. The steric interactions that are introduced upon methyl substitution of the ortho position of BP likely play a crucial role. It is not clear whether the absence of an IE is the result of slow electron exchange equilibration or due to cyanation before dissociation of the initially formed IP.

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Supporting Information Available: Tables of IEs on the photocyanation of BP as a function of the BP and DCN concentration and 2,2′-, 3,3′-, and 4,4′-DMBP as a function of the DMBP concentration. This material is available free of charge via the Internet at http://pubs.acs.org.

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