Isolation and Structure Elucidation of Transient (Colored) Complexes of Arenediazonium with Aromatic Hydrocarbons as Intermediates in Arylations and Azo Couplings

T. M. Bockman, D. Kosynkin, and J. K. Kochi*

Chemistry Department, University of Houston, Houston, Texas 77204-5641

Received March 24, 1997[⊗]

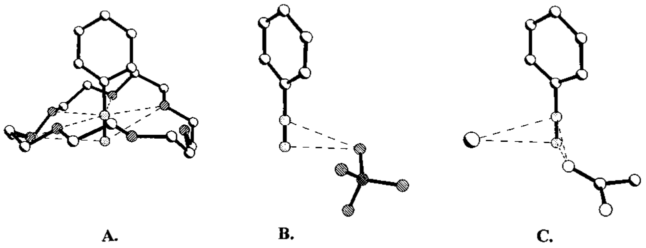
Brightly colored (1:1) complexes are observed immediately upon the mixing of electron-poor arenediazonium (ArN_2^+) salts and aromatic hydrocarbons (ArH). Binding energies of these intermolecular electron donor−acceptor or EDA complexes are typically $\Delta G_{EDA} < 1$ kcal mol^{-1} in acetonitrile. As such, the weak donor−acceptor interaction in [ArN_2^+ ArH] is reminiscent of that in other transient complexes which exhibit charge-transfer (CT) absorption bands of the type originally described by Mulliken. Successful isolation of crystalline (colored) complexes between various ArH/ArN_2^+ pairs allows X-ray crystallography to identify the pertinent donor−acceptor interaction responsible for the distinctive (CT) colors. Indeed, the cofacial stacking of the aromatic donor on top of the aromatic moiety of ArN_2^+ is uniquely different from the usual bonding modes of electron-rich anions directly to the diazono (N_2^+) center. The mechanistic implication of such $\pi-\pi$ interactions of ArH/ArN_2^+ pairs to the transition state for electron-transfer arylation is discussed in its relationship to electrophilic azo coupling.

Introduction

Aromatic or arenediazonium cations (ArN_2^+) show ambivalent behavior toward electron-rich donors, especially when they act either as 2-electron electrophiles or as 1-electron oxidants.[1−3] Inherent to both types of reactivity, $C_6H_5N_2^+$ as the prototypical electron acceptor[4] forms intermolecular complexes with various types of electron donors (D), heretofore designated generically as either an electron donor−acceptor (EDA) complex in electrophilic processes[5] or a precursor complex in electron-transfer processes.[6] As such, complex formation represents the (free) energy well indicative of the mutual recognition of the electron acceptor by the electron donor which is especially relevant prior to bimolecular reactions.[7] Such intermolecular EDA or precursor complexes have been isolated in some cases, but more commonly their existence as preequilibrium intermediates has merely been inferred from spectroscopic changes attendant upon the mixing of the arenediazonium salt with an electron-rich donor.

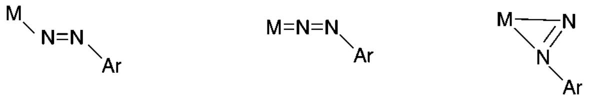
Insofar as structural studies are concerned, crystalline 1:1 molecular complexes of ArN_2^+ with several macrocyclic donors (D = crown ethers) have been isolated, and X-ray crystallography established the nonbonded complexation to derive via the cationic diazono (N_2^+) terminus projecting through the electron-rich cavity (see **A** in Chart 1).[8] In a similar vein, the 1:1 complex of benzenediazonium cation with D = tetrafluoroborate[9] (**B**) is within van der Waals distance from the diazono group, and the solvate (**C**) of benzenediazonium chloride with acetic acid shows both the (nonbonded) chloride ion and carbonyl oxygen within van der Waals contact to the pair of nitrogen atoms,[10] as illustrated in Chart 1.

Chart 1



Complexation of the arenediazonium cation to various electron-rich organometal anionic donors are known to yield aryldiazenido complexes in which the ArN_2 ligand can bind to the metal center (M) via three different modes of coordination[11] as illustrated in Chart 2, the choice of which depends on the metal center and ancillary ligands.[12] It is noteworthy that the doubly bent structure **D** bears the strongest relationship to covalently bonded purely

Chart 2



D (doubly bent) **E** (singly bent) **F** (side on)

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1997.

(1) For reviews, see: Patai, S. Ed. *The Chemistry of Diazonium and Diazo Groups*; Wiley: New York, 1978; Parts 1 and 2.

(2) Zollinger, H. *Diazo Chemistry*, 2nd ed.; VCH: New York, 1994; Vol. 1.

(3) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992.

(4) (a) Based on the reduction potential of $C_6H_5N_2^+$ estimated to be at least 0.8 V. See Elofson, R. M.; Gadallah, F. F. *J. Org. Chem.* **1969**, *34*, 854. (b) Note also that the Hammett substituent constants for the N_2^+ group are highly positive, with $\sigma_m = 1.76$ and $\sigma_p = 1.91$. (c) Kampar, V. E. *Usp. Khim. [Engl. Trans.]* **1982**, *51*, 107.

(5) (a) Kosower, E. *Prog. Phys. Org. Chem.* **1995**, *3*, 81. (b) Colter, A. K.; Dack, M. R. J., *Mol. Complex.* **1973**, *1*, 301; **1974**, *2*, 1.

(6) Cannon, R. D. *Electron Transfer Reactions*; Butterworths: London, 1980.

(7) Kochi, J. K. *Acta Chem. Scand.* **1990**, *44*, 409.

(8) **A** is the perspective view of the EDA complex of *p*-methoxybenzenediazonium tetrafluoroborate and 21- crown-7. (The *p*-methoxy group is deleted for clarity). Groth, P. *Acta Chem. Scand.* **1981**, *A35*, 541.

(9) Cygler, M.; Przybylska, M.; Elofson, R. M. *Can. J. Chem.* **1982**, *60*, 2852.

(10) Romming, C.; Tjornhom, T. *Acta Chem. Scand.* **1968**, *22*, 2934.

(11) (a) Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 1369. (b) Kim, G. C. Y.; Batchelor, F. J.; Yan, X.; Einstein, F. W. B.; Sutton, D. *Inorg. Chem.* **1995**, *34*, 6163.

(12) Sutton, D. *Chem. Rev.* **1993**, *93*, 995.

S0022-3263(97)00540-9 CCC: $14.00

organic structures such as the well-known (stable) azo compounds. However, the search of the wholly organic literature revealed no nonbonded (either stable or transient) complexes with either structure **D** or **E**. The vast majority of the intermolecular complexes of organic origin (like those shown as **A**, **B**, or **C**) are related to the side-on structure **F**. Furthermore, the site of intermolecular complexation of the arenediazonium cation with the donor D is always centered on the diazono nitrogens as the primary seat of cationic charge.[13]

Transient intermolecular complexes of ArN_2^+ with aromatic donors (D = ArH) have been spectrally described as reactive intermediates in electrophilic aromatic substitution (azo-coupling reactions) and they may also be pertinent to aromatic arylation (Gomberg–Bachmann reactions).[14] Related studies have subsequently confirmed the spectral shifts that are diagnostic of intermolecular EDA complexation between arenediazonium acceptors and uncharged aromatic donors,[15,16] *i.e.*

$$ArN_2^+ + ArH \xrightleftharpoons{K_{EDA}} [ArN_2^+, ArH] \qquad (1)$$

Although the brackets enclose the transient EDA complexes, such spectroscopic observations leave unresolved their structural identity. Moreover, aromatic diazonium cations are highly ambiphilic owing to the positive charge that can be extensively delocalized,[17] and ambident reactivity to nucleophilic donors is shown at both the terminal nitrogen atom as well as the (*ortho* and *para*) ring positions.[18] Thus, it is not at all clear from the earlier structural studies (*vide supra*) how the arenediazonium moiety interacts with aromatic donors to form the intermolecular complexes for which the indirect (spectroscopic) evidence is summarized above. Therefore, our first task was to develop general methods for the isolation of these fugitive species in crystalline form suitable for X-ray crystallography. Accordingly, we selected in Chart 3, a graded series of (mono- and disubstituted) benzenediazonium cations as electron-poor acceptors, based on their reduction potentials.[19]

Chart 3

$XC_6H_4N_2^+$ (subst.)	$E_{1/2}$ (V)	$X_2C_6H_3N_2^+$ (subst.)	$E_{1/2}$ (V)
p-Bromo	0.35	3,5-Dicarboethoxy	0.51
p-Carboethoxy	0.48	3,5-Bis(trifluoromethyl)	0.51
m-Nitro	0.48	3,5-Dinitro	0.64
p-Nitro	0.49		

Thus in this study, a span of 7 kcal mol^{-1} separates the weakest from the strongest acceptor by utilizing a moderate electron-withdrawing bromo substituent and a pair of powerful nitro substituents, respectively.

Results

The substituted benzenediazonium cations listed in Chart 3 were prepared as either the tetrafluoroborate or hexafluorophosphate salt by precipitation of ArN_2^+ (conventionally prepared from the appropriate aniline and sodium nitrite)[20] from aqueous solution with HBF_4 or HPF_6.[21] Recrystallization of these arenediazonium salts from diethyl ether mixtures with acetonitrile or acetone yielded colorless crystals, with the exception of the *p*-nitro derivative (pale yellow crystals).

1. Spectral Evidence for the Formation of EDA Complexes of Various ArN_2^+ with Aromatic Hydrocarbons in Solution. When crystalline 3,5-dinitrobenzenediazonium tetrafluoroborate was dissolved in anhydrous acetonitrile, the colorless solution took on a bright yellow (orange) coloration immediately upon the addition of naphthalene. Incremental additions of naphthalene (up to 8 equiv) resulted in the progressive intensification of the yellow color, the quantitative effects of which are illustrated by the series of UV-vis spectra in Figure 1A. The visible (broad) absorption band with λ_{max} = 370 nm (see inset) was not present in either the 3,5-dinitrobenzenediazonium salt or naphthalene alone. The reversible character of the spectral change was demonstrated by the quantitative recovery of the unchanged diazonium salt and the naphthalene donor from the colored (orange) solution, as described in the Experimental Section. Such control experiments obviated any complication arising from other (irreversible) color-forming reactions (such as the well-known azo coupling)[2] on the timescale of the spectral measurements.

A. Charge-Transfer Character of the Intermolecular Complexes. Distinctive color changes were observed with various α-substituted naphthalenes, and the UV-vis absorption spectra typically showed progressive bathochromic shifts in the order: $CH_3 > H > Cl$. Since this trend corresponded to the order of increasing ionization potentials (IP) of the substituted naphthalene,[22] the striking color changes (and spectral shifts) were readily ascribed to the charge-transfer transitions

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[13] For a discussion of which nitrogen is the center of cationic charge, see Wallis, J. D.; Easton, R. J. C.; Dunitz, J. D. *Helv. Chim. Acta* **1993**, *76*, 1411.

[14] Koller, S.; Zollinger, H. *Helv. Chim. Acta* **1970**, *53*, 78.

[15] Kampar, V. E.; Kokars, V. R.; Neiland, O. Ya. *Zhur. Obs. Khim. [Engl. Trans].* **1977**, *47*, 784.

[16] For examples of complexation of ArN_2^+ with anionic donors, see Becker, H. G. O.; Schukat, G.; Kuzmin, M. G. *J. Prakt. Chem.* **1975**, *317*, 229. Jirksky, J.; Fojtik, A.; Becker, H. G. O. *Coll. Czech. Chem. Commun.* **1981**, *46*, 1560. Becker, H. G. O.; Pfeifer, D.; Radeglia, R. *Z. Naturforsch.* **1983**, *38b*, 1591.

[17] Glaser, R. *J. Phys. Chem.* **1989**, *93*, 7993.

[18] For reviews, see Niemeyer, H. M. in ref 1, p 232 ff and Lewis, E. S. in ref 1, p 506.

[19] Owing to the irreversible electrochemical behavior of ArN_2^+, the reduction potentials are given as polarographic $E_{1/2}$ values from Elofson, R. M. and Gadallah, F. F. in ref 4a.

[20] Shank, K. in ref 1, p 645.

[21] March, J. in ref 3, p 671.

[22] (a) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: New York, 1970; p 457. (b) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki T.; Iwata, S. *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules*; Halsted Press: New York, 1981. (c) Kobayashi, S.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1994**, *47*, 2563. (d) See also Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968.

[23] (a) Mulliken, R. S. *J. Am. Chem. Soc.* **1952**, *74*, 811. (b) Mulliken, R. S.; Person W. B. *Molecular Complexes: A Lecture and Reprint Volume;* Wiley: New York, 1969. (c) Hanna, M. W.; Lippert, J. L. In *Molecular Complexes*; Foster, R., Ed.; Crane, Russak: New York, 1973; Vol. 1, p 2 ff.

[24] According to Mulliken,[23] the charge-transfer absorption band ($h\nu_{CT}$) results from the spectral transition (of an electron) from the HOMO of the aromatic donor to the LUMO of the acceptor within the EDA complex, *i.e.*

$$[ArN_2^+, Naph] \xrightarrow{h\nu_{CT}} ArN_2^{\bullet}, Naph^{\bullet+}$$

For a recent summary of the experimental verification of charge-transfer activation by time-resolved spectroscopy, see ref 7.

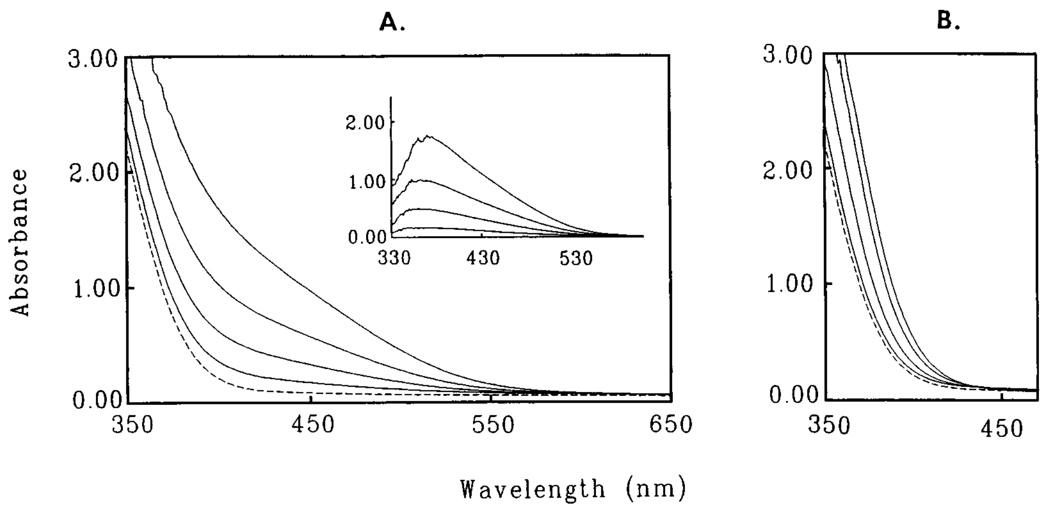


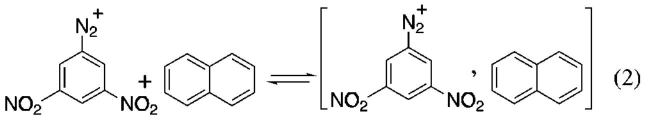
Figure 1. UV-vis absorption of 1.0 × 10^{-2} M 3,5-dinitrobenzenediazonium tetrafluoroborate alone (dashed lines) and with (A) 0.036, 0.10, 0.28, and 0.50 M naphthalene or (B) 0.55, 1.6, 3.9, and 8.4 M benzene. The inset in A shows the difference spectra in which the absorbance of the diazonium cation has been subtracted.

Table 1. Charge-Transfer Absorptions of Aromatic EDA Complexes with Diazonium Cations in Solution[a]

aromatic donor	IP (eV)	λ_{soln}, nm[b] CB	DN
toluene	8.82	367 (3.28)	<400
o-xylene	8.56	410 (3.04)	425
m-xylene	8.56	–	420
p-xylene	8.44	420 (2.95)	465
mesitylene	8.42	425 (2.92)	455
naphthalene	8.12	445 (2.79)	530
p-dimethoxybenzene	7.90	502 (2.47)	–
anisole	8.39	440 (2.84)	–

[a] In acetonitrile containing 0.1 M ArN_2^+ and aromatic donor at 24 °C. [b] For the charge-transfer band (λ_{soln}) in solution, see text. Acceptor: CB = *p*-carbethoxybenzenediazonium tetrafluoroborate and DN = 3,5-dinitrobenzenediazonium hexafluorophosphate. Number in parentheses is the relative charge-transfer energy in eV.

($h\nu_{CT}$) associated with the various reversibly formed EDA complexes, *e.g.*



(2)

according to the expectations of Mulliken theory.[23,24]

Characteristic color changes were also immediately observed when substituted benzene donors were added to a solution of either the 3,5-dinitrobenzenediazonium or *p*-carbethoxybenzenediazonium salt. For example, the addition of benzene (IP = 9.08 eV) induced a color change to pale yellow, while the addition of a stronger donor such as *p*-dimethoxybenzene (IP = 7.90 eV) resulted in a deep red coloration. However, the absorptivity of the EDA complex of 3,5-dinitrobenzenediazonium cation and benzene was considerably lower, and the CT wavelength was blue-shifted relative to those of the naphthalene complex. As a result, only the unresolved low-energy tails of the absorption bands were apparent, as illustrated in Figure 1B.

B. Mulliken Correlation of the Transition Energies. In order to quantitatively assess the transition energy of these and related (benzenoid) complexes, we evaluated the CT bands as relative values of λ_{soln} in Table 1 from the absorption tails as the wavelength at which the absorbance attained an arbitrary extinction coefficient of ϵ_{CT} = 100 M^{-1} cm^{-1}, in a manner originally proposed by Tsubomura and Mulliken.[25] Table 1 also lists values of λ_{soln} for the analogous series of aromatic EDA complexes with the *p*-carbethoxybenzenediazonium cation. In the latter case, the spectral data for a more extensive series of aromatic donors could be collected, owing to the blue-shifted cutoff of the uncomplexed *p*-carbethoxybenzenediazonium (340 nm) relative to that of the 3,5-dinitro analogue (400 nm). The validity of these spectral measurements is illustrated in Figure 2 by the linear correlation of the CT transition energy based on the Mulliken relationship:[26]

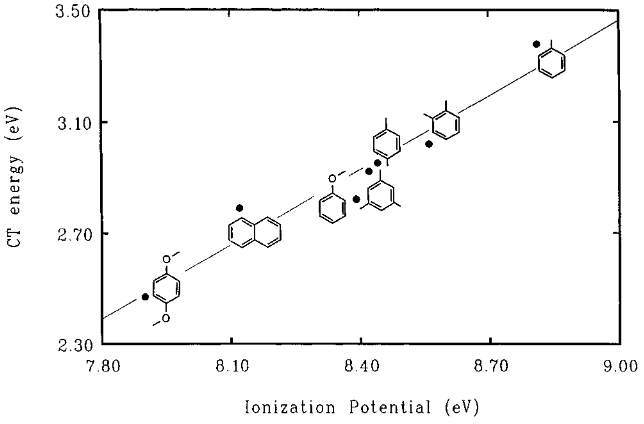


Figure 2. Mulliken correlation of the charge-transfer absorption energy of *p*-carbethoxybenzenediazonium EDA complexes with the ionization potentials of various aromatic donors (as indicated) in acetonitrile solution.

$$hc/\lambda_{soln} = IP - EA - \omega \qquad (3)$$

applicable to a family of related EDA complexes derived from a single acceptor (*i.e.* electron affinity EA and electrostatic work term ω are both invariant).

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[25] (a) Tsubomura, H.; Mulliken, R. S. *J. Am. Chem. Soc.* **1960**, *82*, 5966. (b) See also Rathore, R.; Kochi, J. K. *J. Org. Chem.* **1996**, *61*, 627.

[26] See: Foster, R. *Organic Charge-Transfer Complexes*; Academic: New York, 1969. For the Mulliken relationship: $hc/\lambda_{CT} = h\nu_{CT}$, where *h* is Planck's constant and *c* is the speed of light.

Table 2. Formation Constants of Selected Arenediazonium EDA Complexes with Aromatic Donors in Solution[a]

$XC_6H_4N_2^+$ X	ArH	λ_{soln}, nm	K_{EDA}, M^{-1}	ϵ_{CT}, M^{-1} cm^{-1}	ΔG_{EDA}, kcal mol^{-1}
p-bromo	toluene	340	0.4	400	0.5
p-carbethoxy	*p*-xylene	360	0.2	400	0.9
3,5-dinitro	mesitylene	370	0.4	350	0.5
3,5-bis(trifluoromethyl)	mesitylene	350	0.8	100	0.1
p-bromo	anisole	340	0.4	400	0.5
p-carbethoxy	*p*-methylanisole	400	0.4	250	0.5
p-carbethoxy	*p*-dimethoxybenzene	420	1.0	180	0
3,5-dicarbethoxy	naphthalene	380	0.6	500	0.3
p-carbethoxy	1-chloronaphthalene	400	0.8	200	0.1
p-bromo	1-methylnaphthalene	360	0.3	900	0.7

[a] In acetonitrile containing 0.1 M ArN_2^+ and aromatic donor (ArH) at 24 °C.

2. Binding Energies of Aromatic Complexes with Arenediazonium Cations in Solution. The thermodynamic stability of the various arenediazonium complexes in solution was ascertained by measuring the formation constants K_{EDA} in eq 1 for three classes of aromatic donors (ArH), using the spectrophotometric procedure of Benesi and Hildebrand.[27] Owing to the solubility of the arenediazonium salts in acetonitrile, the charge-transfer absorbance A_{CT} was measured with the selected benzene and naphthalene donors in excess. Under these conditions, the concentration dependence of A_{CT} with varying donor concentration was given by the expresion[28]

$$\frac{[ArN_2^+BF_4^-]}{A_{CT}} = \frac{1}{\epsilon_{CT}} + \frac{1}{K_{EDA}\epsilon_{CT}[ArH]} \quad (4)$$

in which ϵ_{CT} is the extinction coefficient of the complex at the monitoring (CT) wavelength. Since the preliminary investigation indicated rather small (concentration-dependent) changes of A_{CT} indicative of weak complexes, for a given complex we evaluated eq 4 over its entire CT absorption envelope at 2-nm intervals to obtain an averaged value of K_{EDA}, as described in the Experimental Section. The value of K_{EDA} for some selected arenediazonium complexes with methylbenzenes, methoxylated benzenes, and α-naphthalenes are listed in Table 2, together with values of the CT extinction coefficient (ϵ_{CT}) at the monitoring wavelength. Clearly, the magnitudes of the formation constants (column 4) are rather limited, with $K_{EDA} < 1$ M^{-1}, and no well-defined trend among the three classes of aromatic donors.[29] Accordingly, the arenediazonium complexes with aromatic donors were all considered to be uniformly weak, with binding energies $\Delta G_{EDA} < 1$ kcal mol^{-1} in Table 2 (column 6).

3. Isolation of Crystalline EDA Complexes of Arenediazonium Salts and Aromatic Donors. Brightly colored solutions of various combinations of arenediazonium salts (Chart 3) and aromatic donors in anhydrous acetonitrile did not deposit the solid EDA complex, even upon cooling until the solvent froze, at which point the mixture merely turned colorless. Phase separation also occurred when cosolvents such as dichloromethane, diethyl ether, etc. were present, and only the individual (colorless) components could be isolated. An extensive variety of such experiments indicated that the arenediazonium EDA complexes with aromatic donors were too weak (Table 2) to be isolated by direct crystallization from solution.[30]

A. Methodology for Crystal Isolation. We discovered, however, a deposit of bright red crystals when an equimolar solution of 3,5-dinitrobenzenediazonium tetrafluoroborate and naphthalene was left in an open (air) tube for some time. The slow evaporation of acetonitrile led to small amounts of EDA crystals only on the wall immediately above the solution/air interface. In order to exploit this observation to develop a standardized methodology for the difficult isolations, we settled on a large vacuum desiccator in which the fine adjustment of the internal pressure enabled the rate of solvent removal to be carefully controlled (see Experimental Section). This simple procedure allowed various ArN_2^+/ArH combinations to be systematically screened for the formation of crystalline complexes of the appropriate color (Table 1). The colored crystals were redissolved in acetonitrile and then resubjected to the same crystallization procedure until well-formed crystals resulted. The molecular composition was determined spectrophotometrically by quantitative ^1H NMR analysis of a single colored crystal dissolved in acetonitrile-d_3.[31] Donor−acceptor pairs that formed colored crystals were also tested for differing compositions by employing several solutions in which the relative concentrations of the ArN_2^+ salt and ArH were varied over a 100-fold range. By and large, the same integral stoichiometry, crystal habit, and color were observed, irrespective of the relative concentrations of the donor and acceptor.[32]

B. Crystalline EDA Complexes from *p*-Carbethoxybenzenediazonium Hexafluorophosphate. Of the various substituted benzenediazonium salts in Chart 3, the *p*-carbethoxy derivative was the only acceptor that uniformly afforded crystalline complexes from all three classes of aromatic donors.[33] Most noteworthy was the large variability in the molar ratio [A]/[D] of the diazonium acceptor (A) and the aromatic donor (D), which continuously varied from 1:1 (1,2-(methylenedioxy)benzene) to as high as 6:1 (*o*-dimethoxybenzene). Furthermore, the molecular compositions tabulated in Table 3

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[27] Benesi, H. G.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949,** *71,* 2703.

[28] Foster, R. *Mol. Complexes* **1974**, *2*, 107.

[29] Since the Benesi−Hildebrand and related methodologies do not accommodate low values of K_{EDA} very well,[26] the data in Table 1 are subject to considerable (±30%) uncertainty. Thus the trend in K_{EDA} is insufficient to establish structural relationships with certainty.

[30] The crystallization problem is exacerbated by the grossly dissimilar solubilities of the components, such as the hydrophilic diazonium salt in strong contrast to hydrophobic (uncharged) aromatic donor.

[31] The strong downfield shifts of the aromatic protons of ArN_2^+ allowed their ready resolution from those of ArH, sufficient to clearly establish the molecular ratios extant in the crystalline EDA complexes.

[32] For the exception, see the CT crystal of *p*-xylene/*p*-carbethoxybenzenediazonium hexafluorophosphate in which crystallization in the presence of excess *p*-xylene led to the 2A·D complex, whereas crystallization with a tenfold excess of diazonium salt led to the 4A·D stoichiometry.

[33] Crystalline complexes were not observed with this acceptor and either benzene or mesitylene. For the crystallographic explanation of the phenomenon, see Lindeman, S. V. in ref 45b.

Table 3. Crystalline EDA Complexes of Aromatic Donors and *p*-Carbethoxybenzenediazonium Hexafluorophosphate

aromatic donor (D)	IP[a] (eV)	color	mol comp[b]	charge-transfer		infrared
				λ_{xtl}, nm	E_{CT}, eV	ν_{NN}, cm^{-1}
none	–	colorless	A	–	–	2294
toluene	8.82	colorless	4A·D	363	3.42	2297
o-xylene	8.56	colorless	4A·D	388	3.20	2297
m-xylene	8.58	colorless	4A·D	–	–	2297
p-xylene	8.44	yellow	2A·D	419	2.96	2297
mesitylene	8.42	colorless	5A·D	402	3.08	2295
biphenyl	8.27	yellow	3A·D	430	2.88	2301
anisole	8.39	pale yellow	4A·D	420	2.95	2296
m-methylanisole	–	yellow	4A·D	–	–	2295
p-methylanisole	8.18	pale orange	2A·D	477	2.60	2296
3,5-dimethylanisole	–	–	5A·D	–	–	2294
o-dimethoxybenzene	–	pale orange	6A·D	470	2.64	2295
1,2-(methylenedioxy)benzene	–	orange	A·D	490	2.53	2297
p-dimethoxybenzene	7.90	red-orange	2A·D	523	2.37	2289
naphthalene	8.15	yellow	2A·D	–	–	2294
1-methylnaphthalene	7.96	yellow	4A·D	475	2.61	2295
2-methylnaphthalene	7.96	yellow	4A·D	484	2.56	–
1-cyanonaphthalene	–	yellow	2A·D	423	2.96	2295
1-bromonaphthalene	–	yellow-orange	4A·D	442	2.81	2295
1-methoxynaphthalene	–	red	–	514	–	2295

[a] Ionization potentials from ref 22. [b] Molecular composition given as the molar ratio of the carbethoxy acceptor (A) to aromatic donor (D).

Table 4. Crystalline EDA Complexes of Aromatic Donors with 3,5-Dinitrobenzenediazonium and Related Salts

acceptor [a] (A)	donor (D)	IP (eV)	color	mol comp[b]	charge-transfer		infrared
					λ_{xtl}, nm	E_{CT}, eV	ν_{NN}, cm^{-1}
DN	biphenyl	8.27	yellow-orange	A·D	471	2.63	2316
DN	1-bromonaphthalene		orange	A·D	509	2.44	2311
DN	naphthalene	8.12	red	A·D	542	2.29	2307
DN	1-methylnaphthalene	7.96	red	A·D	554	2.24	2307
DN	2-methylnaphthalene	7.92	red	A·D	551	2.25	2310
DN	*p*-dimethoxybenzene	7.90	dark red	2A·D	651	1.90	2310
DC	1-cyanonaphthalene		pale yellow	A·D	*c*	–	2288
DC	1-bromonaphthalene		yellow	A·D	*c*	–	2294
DC	naphthalene	8.12	orange	A·D	*c*	–	2294
DC	1-methylnaphthalene	7.96	orange	A·D	*c*	–	2294
DC	2-methylnaphthalene	7.92	yellow	A·D	*c*	–	2203
MN	*p*-dimethoxybenzene	7.90	red	A·D	*c*	–	–

[a] Acceptors: DN = 3,5-dinitrobenzenediazonium, DC = 3,5-dicarbethoxybenzenediazonium, MN = *m*-nitrobenzenediazonium, as hexafluorophosphate or tetrafluoroborate salt. [b] Molecular composition given as the molar ratio of acceptor to donor. [c] Not measured.

showed no obvious relationship with the donor strength of ArH, as given by its ionization potential (column 2). Interestingly, in the absence of an aromatic donor, the crystallization of *p*-carbethoxybenzenediazonium fluoroborate from an acetonitrile solution afforded only the 1:1 crystalline solvate [$EtO_2CC_6H_4N_2^+BF_4^-$, CH_3CN] described in Table 3 (entry 1).

C. 3,5-Dinitro- and 3,5-Dicarbethoxybenzenediazonium as Strong Acceptors. Even as a rather powerful acceptor, 3,5-dinitrobenzenediazonium was highly selective in the choice of aromatic donors with which it formed crystalline complexes. Thus, the extended π-donors listed in Table 4 were the only ones leading to isolable complexes, the methylbenzenes being singularly ineffective. In contrast to the molecular variability of the *p*-carbethoxybenzenediazonium acceptor toward various naphthalenes (Table 3), the 3,5-dinitrobenzenediazonium acceptor afforded the equimolar 1:1 complexes exclusively (Table 4). The same behavior was also observed with the 3,5-dicarbethoxy and (to a certain extent) the 3-nitro derivative[34] in entries 7–11 and 12, respectively.

D. *p*-Dimethoxybenzene as an Effective Aromatic Donor. As the most electron-rich aromatic donor examined in this study, *p*-dimethoxybenzene afforded a crystalline complex with even the *p*-bromobenzenediazonium cation, as the weakest acceptor. Crystalline complexes were also isolated from *m*- and *p*-nitrobenzenediazonium cations. Indeed, some donor–acceptor combinations from electron-rich/electron-poor pairs (*e.g.* *p*-dimethoxybenzene/3,5-dinitro and 3,5-dimethylanisole/*p*-carbethoxy) reacted irreversibly to afford dark colored (azo) residues, which necessitated the meticulous selection of the individual EDA crystals manually.

4. Solid-State Spectroscopy of Crystalline EDA Complexes of Arenediazonium Salts and Aromatic Donors. A. Electronic Transitions in Charge-Transfer Crystals. The colored crystals obtained in Tables 3 and 4 were examined directly in the solid state by diffuse reflectance spectroscopy, as described in the Experimental Section. In each case, the charge-transfer transition was observed as a broad (absorption) band that tailed into the visible region. Indeed, Figure 3 shows the progressive bathochromic shifts of the low-energy tails of the crystalline EDA complexes of *p*-carbethoxybenzenediazonium tetrafluoroborate and aromatic donors in the order: toluene < xylene < mesitylene < methoxytoluene < dimethoxybenzene.

For the quantitative evaluation of the spectral changes, the charge-transfer transition was arbitrarily taken as wavelength λ_{xtl} at which the inflection of the absorbance

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(34) *m*-Nitrobenzenediazonium also formed crystalline complexes with *p*-dimethoxybenzene, but they were not analyzed further.

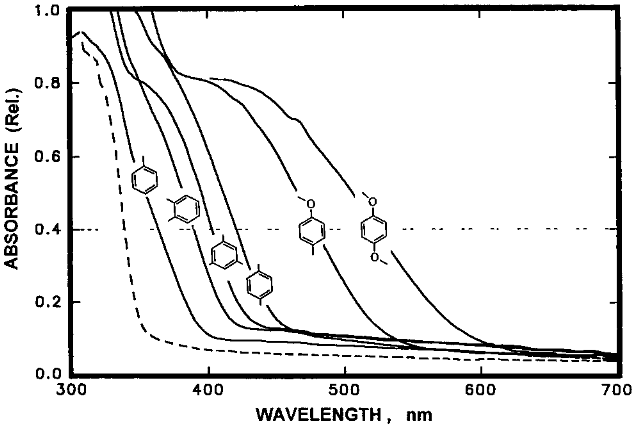

Figure 3. Charge-transfer absorption (low-energy tails) from crystalline *p*-carbethoxybenzenediazonium EDA complexes with various aromatic donors (as indicated) by diffuse reflectance spectroscopy showing progressive bathochromic shifts. The dashed line is the local absorption of the uncomplexed acceptor alone.

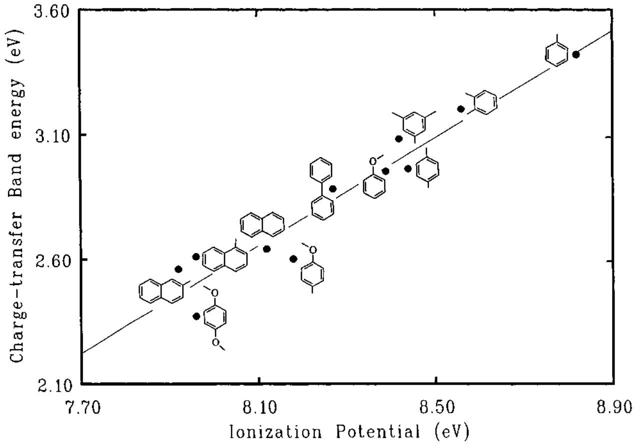

Figure 4. Linear Mulliken correlation of the charge-transfer energy of crystalline EDA complexes of *p*-carbethoxybenzenediazonium cation with the ionization potentials of various aromatic donors (as indicated).

occurred (see Figure 3).[25] The validity of such an assignment is underscored by the linear (Mulliken) plot in Figure 4 of the charge-transfer energy (hc/λ_{xtl}) versus the ionization potential of the aromatic donors listed in Table 3.

B. N−N Vibrational Spectra of Charge-Transfer Crystals. In crystalline arenediazonium salts, the characteristic N−N stretching bands occur in the infrared spectra in a rather narrow range (27 cm^{-1}) from ν_{NN} = 2292 cm^{-1} for benzenediazonium as a weak acceptor to 2319 cm^{-1} for the 3,5-dinitro derivative, as the strongest (Table 5). Thus, it may not be unexpected that the values of ν_{NN} in the various aromatic EDA complexes of the *p*-carbethoxybenzenediazonium cation are essentially invariant (see Table 3, column 7). It is noteworthy that the values of ν_{NN} in the crystalline EDA complexes with the strongest acceptor (3,5-dinitrobenzenediazonium) in Table 4 show a small but distinct upward trend with the donor strength of ArH.

5. X-ray Crystallography of Crystalline EDA Complexes of Arenediazonium Salts and Aromatic Donors. The successful isolation of crystalline EDA complexes in Table 3 and 4 allowed the well-formed colored (single) crystals to be examined directly for structure studies as follows.

Table 5. Infrared (N−N) Frequencies of Substituted Benzenediazonium Salts in the Solid State[a]

substituent	σ^b	ν_{NN}	substituent	σ^b	ν_{NN}
none	0	2292	*p*-nitro	0.78	2299
p-chloro	0.23	2272	3,5-difluoro-2,4,6-trichloro	−	2294
p-bromo	0.23	2272	pentafluoro[c]	−	2314
p-benzoyl	−	2291	3,5-bis(trifluoromethyl)	0.86[d]	2313
p-carbethoxy	0.45	2294	3,5-dinitro[c]	1.42[d]	2319
m-nitro	0.71	2300			

[a] As the hexafluorophosphate salt, unless indicated otherwise. [b] Hammett σ constant. [c] Tetrafluoroborate salt. [d] Additivity assumed.

A. *p*-Carbethoxybenzenediazonium EDA Complexes. For the X-ray crystallographic investigation, we initially selected four *p*-carbethoxybenzenediazonium complexes from Table 3 with widely different donor structures, CT colors, and molecular compositions, *viz.* those with D = toluene (entry 2), (methylenedioxy)benzene (entry 13), and *p*-xylene (entry 5), together with the acetonitrile solvate (entry 1) to serve as the reference structure. The pertinent X-ray data have been deposited with the Cambridge Crystallographic Data Centre,[35] but suffice it to indicate here that we found the aromatic EDA complexes to be comprised of donor−acceptor pairs,[36] in which the structure of each component was the same as that found in the uncomplexed state. For example, the *p*-carbethoxybenzenediazonium acceptor in each of the four crystals contained the same characteristically distorted benzenoid ring, in which the hexagonal symmetry was reduced to two-fold symmetry by a widened internal angle of α = 125 ± 1° at the ipso (N_2^+) carbon and concomitant narrowing of the ortho angles to β = 116 ± 1°.[37,38] Similarly, the aromatic donor moieties consisting of toluene, (methylenedioxy)benzene, and *p*-xylene retained the structures previously found in their native states.[39]

Most pertinent to the diagnostic charge-transfer colors of the aromatic EDA complexes described in Table 3 are the donor−acceptor orientations of the aromatic hydrocarbon (D) relative to the *p*-carbethoxybenzenediazonium cation (A). For purposes of clarity, we focussed on the pairwise donor−acceptor interactions extant in nearest neighbors. Thus, Figure 5 (drawn to scale) shows the essential charge-transfer interaction in aromatic EDA

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(35) University Chemical Lab, Lensfield Rd, Cambridge CB2 1EW, United Kingdom.

(36) In order to focus on the charge-transfer (color) interactions, we will deal here with only those ArN_2^+ and ArH that constitute nearest neighbors.[45b]

(37) Such deformations are common to all diazonium cations whose structures have been crystallographically determined. See: (a) Sorriso, S. in ref 1, p 95. (b) Ball, R. G.; Elofson, R. M. *Can. J. Chem.* **1985**, *63*, 332. (c) Barnes, J. C.; Butler, A.; Anderson, L. *Acta Crystallogr.* **1990**, *C46*, 945. (d) Horan, C. J.; Barnes, C. L.; Glaser, R. *Acta Crystallogr.* **1993**, *C49*, 507. (e) Alcock, N. W.; Greenhough, T. J.; Hirst, D. M.; Kemp, T. J.; Payne, D. R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 8. (f) Sasvari, K.; Hess, H.; Schwarz, W. *Cryst. Struct. Commun.* **1982**, *11*, 781. (g) Cygler, M. et al. in ref 9.

(38) More generally, these values of α and β are characteristic for aromatic carbon centers attached to electron-withdrawing groups. The origin of these structural changes has been discussed, and they are correctly reproduced by theoretical (*ab initio*) calculations. See Domenicano, A.; Vaciago, A. Coulson, C. A. *Acta Crystallogr.* **1975**, *B31*, 1630 and Horan, C. J.; Barnes, C. L.; Glaser, R. *Chem. Ber.* **1993**, *126*, 243. Aside from these deformations, the bond lengths (1.37−1.39 Å) and angles (120°) of the aromatic portion of the diazonium cation do not deviate significantly from the values associated with simple arenes.[39]

(39) (a) Bacon, G. E.; Curry, N. A.; Wilson, S. A. *Proc. Roy. Soc. London, Ser. A* **1964**, *279*, 98. (b) Ghosh, P. N.; Ha, T.-K. *J. Mol. Struct. (THEOCHEM)* **1990**, *206*, 287. (c) Allen, F. H.; Kinnard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. G. *J. Chem. Soc., Perkin Trans. 2* **1987**, 51.

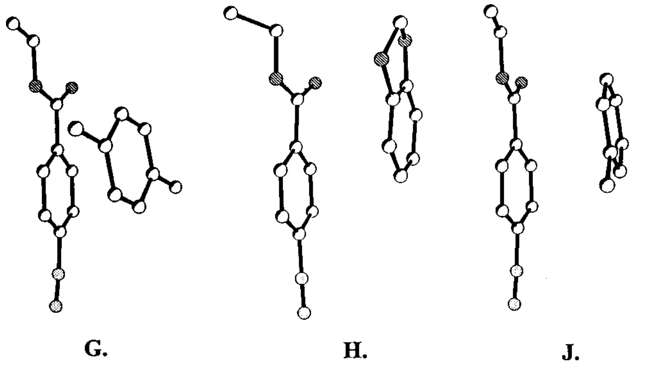

Figure 5. Perspective views of donor–acceptor pairs from the X-ray crystallography of the crystalline *p*-carbethoxybenzenediazonium EDA complexes with (**G**) *p*-xylene, (**H**) methylenedioxybenzene, and (**J**) toluene, showing the cofacial placement of the aromatic donor (ArH) over the carbon π-framework of the diazonium acceptor (ArN_2^+).

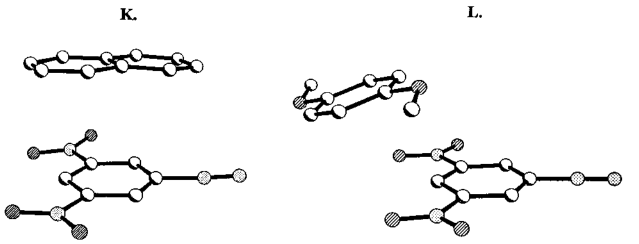

Figure 6. The π–π stacking of (**K**) naphthalene and (**L**) *p*-dimethoxybenzene on the aromatic portion of the 3,5-dinitrobenzenediazonium acceptor in the crystalline EDA complexes, as established by X-ray crystallography.

complexes with arenediazonium to derive from the same π–π interactions of the aromatic donor and acceptor chromophore, the average interplanar separation $d = 3.6 \pm 0.2$ Å, which is essentially that (3.4 Å) generally found in stacked aromatic ring systems.[40]

B. 3,5-Dinitrobenzenediazonium EDA Complexes. As a more powerful acceptor, 3,5-dinitrobenzenediazonium cation formed a series of more highly colored EDA complexes (Table 4), relative to those obtained with the weaker *p*-carbethoxybenzenediazonium acceptor (see Chart 3). From among these, we selected for X-ray crystallographic study those charge-transfer crystals with D = naphthalene and *p*-dimethoxybenzene owing to their intense red and dark red colors, respectively. The structure of the 3,5-dinitrobenzenediazonium acceptor in both EDA crystals consisted of the same highly distorted benzenoid ring ($\alpha = 126°$ and $\beta = 118°$) as found in the carbethoxybenzenediazonium crystals described above. Similarly, the naphthalene and dimethoxybenzene donor moieties were structurally (and conformationally) the same as those found in the uncomplexed donors.[41]

The cofacial orientations of the naphthalene and *p*-dimethoxybenzene donors relative to the 3,5-dinitrobenzenediazonium acceptor in the charge-transfer crystals, as illustrated by the crystallographic views in Figure 6, are essentially the same as these presented for the *p*-carbethoxy analogue in Figure 5. Despite the slight tilt of the *p*-dimethoxybenzene donor moiety, the average interplanar separation of the aromatic donor and acceptor moieties in the red CT crystals are akin to those described in Figure 5.[42] Most notably, the extended π-system of the naphthalene donor allows it to extend over almost the entire diazonium acceptor.

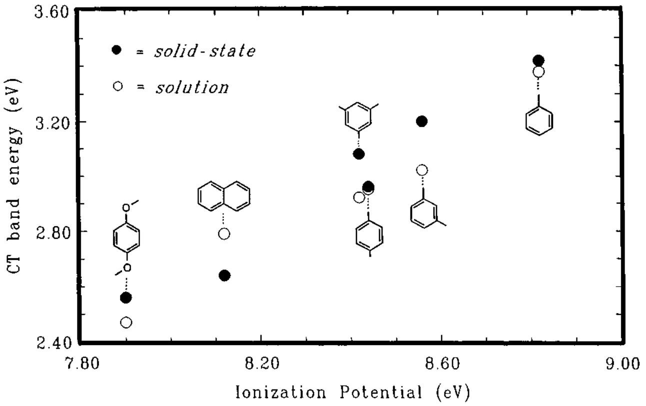

Figure 7. Comparison of the charge-transfer energies of *p*-carbethoxybenzene-diazonium EDA complexes with various aromatic donors (as indicated) in acetonitrile solution and in the crystalline solid state.

Discussion

Aromatic or arenediazonium (ArN_2^+) like tropylium ($C_7H_7^+$) are both electron-poor, coordinatively unsaturated cations and thus rather unusual insofar as stable organic species are concerned.[43] To extend the comparison further, we now find that various ArN_2^+ form an extensive series of electron donor or EDA complexes with aromatic donors (ArH) analogous to those of $C_7H_7^+$ recently reported.[44] As such, we wonder how the structure elucidation of such EDA complexes can be pertinent to the ambiphilic reactivity of ArN_2^+ toward ArH. In particular, we ask whether the recognition of ArN_2^+ by the aromatic substrate in the preequilibrium complexation (eq 1) is indicative of its subsequent chemical behavior in solution.

1. Charge-Transfer Structure of the Donor–Acceptor Pair from Arenediazonium and Aromatic Hydrocarbons. Aromatic EDA complexes of ArN_2^+ like those of $C_7H_7^+$ are characterized in (acetonitrile) solution by charge-transfer or CT absorption bands that undergo diagnostic spectral (color) shifts with the donor strength of ArH. Moreover, the parallel trend of these spectral shifts in solution (Table 1) with those measured in the crystalline EDA complexes (Tables 3 and 4) indicate that the charge-transfer interaction of the ArH/ArN_2^+ pair dissolved in solution is essentially that of the same donor–acceptor pair immobilized in the solid state (see Figure 7). As such, the perspective views in Figure 5 and 6 uniformly depict the cofacial π–π disposition of the aromatic donor (ArH) relative to the arenediazonium cation that is responsible for the charge-transfer colors,

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(40) (a) Potenza, J.; Mastropaolo, D. *Acta Crystallogr.* **1975**, *B37*, 2527. (b) Iball, J.; Low, J. N. *Acta Cryst.* **1974**, *B30*, 2203. See also ref 41b.

(41) (a) Gerzain, M.; Buchanan, G. W.; Driega, A. B.; Facey, G. A.; Enright, G.; Kirby, R. A. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2687. (b) Brock, C. P.; Dunitz, J. D. *Acta Crystallogr.* **1982**, *B38*, 2218.

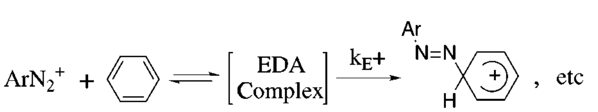
(42) Otherwise, the X-ray crystallography does not distinguish the donor-acceptor interactions extant in the carbethoxybenzenediazonium EDA complexes from those involving the strongest acceptor (*i.e.*, the 3,5-dinitro analogue). However, we note that the aromatic donors are crystallographically disordered in the carbethoxydiazonium crystals whereas they are essentially not disordered in the dinitrodiazonium crystals. The latter suggests that the intermolecular forces are stronger in the CT crystals of the stronger acceptor.

(43) See: le Noble, W. J. *Highlights of Organic Chemistry*; Dekker: New York, 1973; p 692 f.

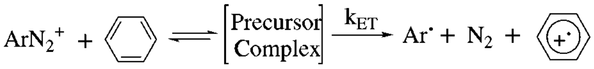
(44) Takahashi, Y.; Sankararaman, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 2954.

both in solution and in the crystal.[45] Such a molecular structure of the EDA complex is adhered to by all aromatic donors (irrespective of their ionization potential) and by weak (carbethoxy) as well as strong (dinitro) benzenediazonium acceptors.[46] It is especially noteworthy that the consistent patterns of donor−acceptor complexation places ArH directly over the carbon π-framework of ArN_2^+, in strong contradistinction to that found (Chart 1) in stable complexes. In other words, the aromatic donors always sense the charge-transfer region of lowest (delocalized) electron density to be located on the aromatic moiety as opposed to the diazono (N_2^+) function.[47] In this regard, the aromatic EDA complexes of ArN_2^+ are analogous to those of other delocalized acceptor cations such as tropylium and methylviologen.[48]

2. Implications of the Charge-Transfer Structure to Diazonium Reactivity. Arenediazonium cations exhibit two distinct patterns of reactivity. On one hand, nucleophiles (Nu) react at the diazono group to form azo products in which the N=N linkage is retained (ArN=N−Nu).[2] Included in such azo couplings is the rate-limiting formation (k_E^+) of the Wheland intermediate[14] (eq 5) that is commonly described as an electrophilic aromatic substitution.[49] On the other hand, a more important class of dediazoniation processes are included among the Sandmeyer, Gomberg−Bachmann, Meerwein, and Schiemann transformations,[50] in which the rate-limiting electron-transfer (k_{ET}) is rapidly followed by the loss of dinitrogen[51,52] (eq 6)



(5)



(6)

The mechanisms in eqs 5 and 6 include the preequilibrium formation of the EDA and precursor complexes, respectively, as traditionally formulated.[5,6] In such intermolecular complexes, the precoordination of the ArH donor to the ArN_2^+ acceptor at the diazono group (compare Chart 1) *versus* the aromatic ring is to be associated with the transitions states for nucleophilic and electron-transfer reactivity in azo coupling (eq 5) and arylation (eq 6), respectively. On this basis, the $\pi-\pi$ interactions in Figures 5 and 6 are those inherent to electron transfer in which the HOMO of ArH senses the extensively delocalized LUMO of ArN_2^+. The importance of delocalized LUMOs in the electron-transfer reactivity of tropylium and methylviologen cations have been confirmed by time-resolved spectroscopy both in the solid state and in solution.[44,53] By way of contrast, the complexation of ArN_2^+ at the terminal diazono group appears to be favored by anionic nucleophiles (*e.g.* BF_4^- and Cl^- in Chart 1) in which electrostatic binding may be the dominant factor.[54] Alternatively stated, small anions as *hard* nucleophiles may prefer the relatively *hard* diazono site as opposed to the preference of the relatively *soft* aromatic donors (ArH) relevant to aromatic dediazoniation.

Summary and Conclusions

Aromatic diazonium cations ArN_2^+ rapidly interact with aromatic hydrocarbons (ArH) to form transient electron donor−acceptor or EDA complexes in acetonitrile solutions, but they can be isolated as crystalline (colored) complexes. X-ray crystallography reveals that the aromatic donor ArH interacts directly with the aromatic face of ArN_2^+ via direct $\pi-\pi$ (nonbonded) coordination and not to the pendant diazono (N_2^+) moiety, as previously found in stable structures of ArN_2^+ with various anionic and crown ether donors.[8−10] As such, the cofacial structures **G**−**L** of aromatic donors with diazonium cations in Figures 5 and 6 are best considered to be the precursor complexes for electron-transfer activation of ArN_2^+ (leading to the Gomberg−Bachmann and related dediazoniation processes) in eq 6. By contrast, the diazono structures **A**−**E** in Charts I and II relate more to the EDA complexes pertinent to electrophilic aromatic substitution (*i.e.* azo coupling) in eq 5.

Experimental Section

Materials. Benzene, toluene, *o*- and *m*-xylenes (EM Science), mesitylene, anisole, *o*- and *p*-dimethoxybenzene (Aldrich) were purified by twofold distillation under an atmosphere of argon. Naphthalene (Matheson) and *p*-dimethoxybenzene were recrystallized from ethanol and sublimed *in vacuo.* *p*-Xylene (Kodak) was purified by repeated partial freezing (five times) and distilled from sodium under an argon atmosphere. Acetonitrile (OmniSolv, EM Science was transferred to a Schlenk flask under an argon atmosphere and used without further purification. Dichloromethane (HPLC grade, EM Science) was initially stirred with concentrated sulfuric acid; the separated layer was neutralized, dried over anhydrous Na_2CO_3, and finally distilled from anhydrous P_2O_5 under an argon atmosphere. Absolute ether, ethyl acetate, and chloroform (Reagent grade, EM Science) were used without further purification. Deuterated solvents for the NMR experiments (Aldrich) were stored over molecular sieves prior to use.

Preparation of the Diazonium Salts. In a typical procedure,[55] a solution of the appropriate aniline (0.06 mol) in concentrated HCl (50 mL) contained in a 250-mL beaker was cooled in a dry-ice bath until it began to freeze. An ice-cold solution of sodium nitrite (5.6 g, 0.08 mol) was then added with stirring. Cooling and stirring were continued until the solution became clear. Activated charcoal (0.5 g) was added, and the mixture was filtered through a pad of Celite. The clear yellow filtrate was treated with 60% aqueous HPF_6 (5 mL) to

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(45) (a) Figures 5 and 6 illustrate only the nearest neighbor interactions of ArN_2^+ and ArH. The other more distant interactions are included with the full crystallographic presentation of the extensive ArN_2^+/BF_4^- or PF_6^- network. (b) Lindeman, S. V., manuscript to be submitted.

(46) Small lateral displacements along the aromatic planes are not expected to be important factors in the charge-transfer transitions. See: (a) Staab, H. A.; Reibel, W. R. K.; Krieger, C. *Chem. Ber.* **1985**, *118*, 1230. (b) Volger, H.; Schanne, L.; Staab, H. A. *Chem. Ber.* **1985**, *118*, 1254.

(47) Extensive delocalization of the positive charge of ArN_2^+ onto the aromatic moiety is in line with electron-density calculations. See: Glaser, R.; Horan, C. J. *J. Org. Chem.* **1995**, *60*, 7518.

(48) See: Yoon, K. B.; Kochi, J. K. *J. Am. Chem. Soc.* **1991**, *95*, 3780.

(49) Taylor, R. *Electrophilic Aromatic Substitution*, Wiley: New York, 1990; p 278 ff.

(50) (a) Cowdrey, W. A.; Davies, D. S. *Chem. Soc. Quart. Rev.* **1952**, *6*, 358. (b) Cohen, T.; Lewarchik, R. J.; Tarino, J. Z. *J. Am. Chem. Soc.* **1974**, *96*, 7753. Rondestvedt, C. S. *Org. React.* **1960**, *11*, 189. (c) Gomberg, M.; Bachmann, W. E. *J. Am. Chem. Soc.* **1924**, *46*, 2339. (d) Bachmann, W. E.; Hoffman, R. A. *Org. React.* **1944**, *2*, 224. (e) DeTar, D. F. *Org. React.* **1957**, *9*, 409. (f) Pschorr, R. *Chem. Ber.* **1896**, *29*, 496. (g) Abramovitch, R. A. *Adv. Free Radical Chem.* **1966**, *2*, 4787.

(51) See: (a) Galli, C. *Chem. Rev.* **1988**, *88*, 765. (b) Via the rapid homolysis of the aryldiazenyl radical, see: Suehiro, T. *Rev. Chem. Intermed.* **1988**, *10*, 101.

(52) Kosynkin, D.; Bockman, T. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 4846.

(53) Hubig, S. M.; Kochi J. K. *J. Phys. Chem.* **1995**, *99*, 17578.

(54) The structural consequences of such ion-pair interactions in the extensive two-dimensional networks will be described in detail.[45b]

(55) Roe, A. *Org. React.* **1949**, *5*, 193.

give a fine precipitate of the diazonium hexafluorophosphate. The precipitate was filtered, washed with aqueous HPF_6 and water, and dried at room temperature *in vacuo* (0.3 torr). The crude diazonium salt was recrystallized from an acetonitrile/diethyl ether or an acetone/diethyl ether solution.

***p*-(Ethoxycarbonyl)benzenediazonium Hexafluorophosphate.**[56] Colorless crystals (16.6 g, 86%) from ethyl 4-aminobenzoate (9.90 g, 0.06 mol). The colorless salt was recrystallized from acetone/ether. ^{1}H NMR (CD_3CN) δ 8.575 (m, 2H), 8.415 (m, 2H), 4.420 (q, 2H, $J = 7.2$ Hz), 1.380 (t, 3H, $J = 7.2$ Hz); ^{13}C NMR (CD_3CN) δ 164.2, 142.7, 133.8, 132.9, 119.2, 63.9, 14.3. The ^{1}H, ^{13}C and ^{19}F NMR spectra were measured on a General Electric QE-300 FT-NMR spectrometer with internal $(CH_3)_4Si$ or external CF_3COOH standards.

***m*-Nitrobenzenediazonium Hexafluorophosphate.**[57] Colorless needless (13.0 g, 74%) from 3-nitroaniline (8.38 g, 0.06 mol). The salt was recrystallized from acetonitrile/ether. ^{1}H NMR (CD_3CN) δ 9.256 (t, 1H, $J = 2.1$ Hz), 8.955 (dd, 1H, $J_1 = 9.3$ Hz, $J_2 = 2.1$ Hz), 8.791 (dd, 1H, $J_1 = 9.3$ Hz, $J_2 = 2.0$ Hz), 8.172 (t, 1H, $J = 9.3$ Hz).

***p*-Nitrobenzenediazonium Hexafluorophosphate.**[56,58] Pale yellow needles (13.6 g, 78%) from 4-nitroaniline (8.28 g, 0.06 mol). ^{1}H NMR (CD_3CN) δ 8.760 (m, 2H), 8.645 (m, 2H); ^{13}C NMR (CD_3CN) δ 155.4, 135.4, 127.7, 121.4.

3,5-Bis(ethoxycarbonyl)benzenediazonium Hexafluorophosphate.[59] Colorless crystals (18.0 g, 76%) from diethyl 5-aminoisophthalate (14.2 g, 0.06 mol). ^{1}H NMR (CD_3CN) δ 9.249 (d, 2H, $J = 1.2$ Hz), 9.133 (t, 1H, $J = 1.2$ Hz), 4.472 (q, 2H, $J = 7.1$ Hz), 1.419 (t, 3H, $J = 7.1$ Hz); ^{13}C NMR (CD_3CN) δ 162.8, 142.0, 137.0, 135.6, 64.2, 14.3.

3,5-Bis(trifluoromethyl)benzenediazonium Hexafluorophosphate.[60] Colorless crystals (16.7 g, 72%) from 3,5-bis(trifluoromethyl)aniline (13.6 g, 0.06 mol) as described above. ^{1}H NMR (CD_3CN) δ 9.07 (broad s, 1H), 8.86 (broad s, 2H); ^{13}C NMR (CD_3CN) δ 136.9 (t, $J = 4.7$ Hz), 135.3 (q, $J = 36$ Hz), 134.6 (t, $J = 4.7$ Hz), 12.3 (q, $J = 274$ Hz), 116.9.

3,5-Dinitrobenzenediazonium Tetrafluoroborate.[60] Colorless flakes (13.5 g, 80%) from 3,5-dinitroaniline. IR (KBr) 3102, 3090, 3079, 3042, 2319, 1616, 1605, 1557, 1352, 1105, 1082, 1035, 1024, 998, 925, 899; ^{1}H NMR (CD_3CN) δ 9.619 (d, 2H, $J = 1.8$ Hz), 9.506 (t, 1H, $J = 1.8$ Hz); ^{13}C NMR (CD_3CN) δ 150.1, 133.6, 131.6, 119.7. *Caution should be used in handling this material due to its potentially explosive nature.*[61]

Charge-Transfer Spectra of Aromatic EDA Complexes with Diazonium Cations in Solution. A solution of the aromatic diazonium tetrafluoroborate or hexafluorophosphate (1.0×10^{-3} M) was prepared in acetonitrile (4.0 mL) and transferred to an argon-purged quartz curvette (optical path length 1.0 cm), and the UV-vis spectrum of the solution was measured on a Hewlett-Packard 8450A diode-array spectrometer with 2 cm^{-1} resolution. The aromatic donor was added in increments of 0.1 to 1.0 mmol, and the UV-vis spectrum was remeasured after each addition. The operation was repeated six times. The data was processed using the program SigmaPlot as follows: First, the spectral absorbance of the diazonium salt was subtracted from the seven spectra of the arene/diazonium complexes. From the subtracted spectra, a value for the formation constant (K), its standard deviation (σ), and the extinction coefficient (ϵ) was calculated for each data point (every 2-nm) using the Benesi−Hildebrand approximation.[28] The values of K and ϵ were plotted as a function of the wavelength. The value of K was judged to be meaningful at a given wavelength if K was greater than σK. The values of K in Table 1 represented the averages for each wavelength at which a meaningful K could be extracted. Since the charge-transfer bands were featureless tailing bands, the band maximum was not available as a criterion of the charge-transfer energy. Attempts to determine the inflection point (*vide infra*) were not successful since the calculated second derivative, $d^2A/d\lambda^2$, did not go to zero in the 350−700 nm spectral region. To obtain a measure of the charge-transfer transition energy, the extinction coefficient of the CT band (ϵ_{CT}) was plotted as a function of the wavelength, and the wavelength at which ϵ_{CT} reached a value of 100 (λ_{soln}) was taken as the measure of the charge-transfer wavelength.

Formation of Crystalline EDA Complexes from Aromatic Donors and Substituted Benzenediazonium Salts. The donor/diazonium pairs which showed no change in their UV-vis spectra (over the course of 10 min when dissolved in acetonitrile) were judged to be sufficiently stable for screening. Mixed solutions of the diazonium salt (0.1 mmol) and the aromatic donor (10 mmol) were prepared in acetonitrile (0.5 mL) and transferred to 2-dram vials. The vials were placed in a vacuum desiccator, which was slowly evacuated so that the solutions in the vials did not bubble. After about 1 h, the wet crystalline residues were examined with the aid of a microscope, and the presence of colored crystals was regarded as a positive criterion for complex formation. If the initial examination of the residue indicated possible (but not certain) formation of colored complexes, the evaporation and examination procedure was repeated with 1.0 mmol of diazonium salt and 100 mmol of donor, dissolved in a minimum amount of acetonitrile. Donor−acceptor pairs which formed colored crystals in the initial screening phase were tested for differing composition. Two solutions were prepared in 0.5 mL of acetonitrile as follows. Solution 1, consisted of 0.10 mmol of diazonium salt and 1.0 mmol of donor, and solution 2 consisted of 1.0 mmol of diazonium salt and 0.10 mmol of donor. The solvent was removed by evacuation over the course of about 1 h (*vide supra*), and the colored crystalline residue was examined visually with the aid of a microscope. In all but one case, the habit and color of the crystals obtained from the two solutions were the same. However, the solution of *p*-xylene and *p*-carbethoxybenzenediazonium hexafluorophosphate containing the acceptor in excess (solution 2) deposited yellow crystals, while the crystals formed from the solution containing excess donor (solution 1) were colorless.

In order to check for reversibility, a solution of naphthalene (12.8 mg, 0.1 mmol) and 3,5-dinitrobenzenediazonium tetrafluoroborate (28.3 mg, 0.1 mmol) in acetonitrile (1 mL) was kept for 1 h at room temperature in the dark and then evaporated to dryness *in vacuo*. The bright orange-red residue thus obtained was triturated with $CHCl_3$ (ethanol-free, 3×0.5 mL) to leave a colorless solid. The solid was dried *in vacuo* (27.5 mg recovered) and analyzed by ^{1}H NMR in CD_3CN to show the exclusive presence of the original diazonium salt. The chloroform extracts were evaporated *in vacuo* at 0 °C to yield a colorless residue (12.0 mg) which was analyzed by ^{1}H NMR and GC-MS to contain naphthalene only. Reversibility of the complex formation (absence of colored products) in the other donor−acceptor pairs listed in Tables 2 and 3 were studied by the same method. However, it should be noted that only a few of the donor−acceptor pairs formed colored crystalline EDA complexes under these conditions. Most often, the evaporation of the colored solution resulted in a colorless residue. Highly volatile donors (benzene, toluene, and xylenes) were lost with the solvent, and thus were not quantified.

Charge-Transfer Spectra of Crystalline EDA Complexes. The crystalline colored crystals were ground together with a 100-fold excess of NaCl, and the resulting powder was used for the spectral measurements. [Dispersions in either alumina or silica were not stable, and their spectra changed during the measurement]. The diffuse reflectance spectra were measured on a Perkin-Elmer 330 UV-vis spectrometer equipped with a Hitachi 210-2101 integrating sphere. The output was digitized using a Microtek IIsp digital scanner at a resolution of 1-nm per datapoint, and the data was processed using the SigmaPlot software. The raw absorbance data, $A(\lambda)$, was first smoothed over a 7-point range, and the first deriva-

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tive (dA/dλ) was calculated from the smoothed data. The first derivatives were smoothed (over a 7-point range), and the second derivative was calculated. [Smoothing and differentiation were performed using internal routines in SigmaPlot]. The wavelength on the red edge of the CT absorption band at which d^2A/dλ^2 went to zero was the inflection wavelength (λ_{xtl}) in Tables 3 and 4.

The infrared spectra of the crystalline complexes were recorded in transmission mode on either a Nicolet 10 DX or 560 FT-IR spectrometer. The crystals were ground with mineral oil (Nujol), and the resulting dispersions were subjected to spectral analysis. The N═N stretching vibrations in Table 5 corresponded to absorptions in the range 2270 to 2320 cm^{-1}.

Preparative-Scale Synthesis of the Crystalline EDA Complexes. The aromatic diazonium salt (5.00 mmol) and the aromatic donor were dissolved in a minimum quantity of acetonitrile, and the solution was transferred to a 50-mL Teflon beaker. The beaker was placed in an argon-filled vacuum desiccator, which was then slowly evacuated with the aid of a precision needle valve. After 12 h of evacuation, the colored crystals were collected from the mother liquor. A few of these crystals were redissolved in acetonitrile and subjected to the same crystallization procedure. For the determination of the compositions in Tables 3 and 4, a single colored crystal (~20 mg) was dissolved in acetonitrile-d_3 and analyzed by ^{1}H-NMR spectroscopy (*vide supra*). Some donor−acceptor pairs reacted to form dark-colored products (*i.e.* not EDA complexes) and thus were "too reactive" for the standard screening procedure. These pairs were *p*-dimethoxybenzene/3,5-dinitrobenzenediazonium and 3,5-dimethylanisole/4-carbethoxybenzenediazonium. In such cases, the desired EDA crystals had to be separated by hand from a mass of dark-colored product material.

X-ray Crystallography of Crystalline EDA Complexes of Arenediazonium Salts and Aromatic Donors. In order to examine the donor−acceptor interactions in charge-transfer complexes, four of the crystalline *p*-carbethoxybenzenediazonium samples were selected from Table 3 with donors D = acetonitrile (entry 1), toluene (entry 3), (methylenedioxy)benzene (entry 13), and *p*-xylene (entry 5), and two from the 3,5-dinitrobenzenediazonium complexes in Table 4 with D = naphthalene (entry 3) and *p*-dimethoxybenzene (entry 6). X-ray crystallography was performed on a Nicolet R3m/V automatic diffractometer at −50 °C, and the relevant data of the six charge-transfer crystals for structures **G**−**L** and that of the acetonitrile solvate have been deposited and can be obtained from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 - 1EZ, U.K.

Acknowledgment. We thank S. V. Lindeman and J. D. Korp for crystallographic assistance, and the National Science Foundation and the R. A. Welch Foundation for financial assistance.

JO970540N