B

Organic Electron Transfer Systems, II[1]

Substituted Triarylamine Cation-Radical Redox Systems – Synthesis, Electrochemical and Spectroscopic Properties, Hammet Behavior, and Suitability as Redox Catalysts

Steffen Dapperheld, Eberhard Steckhan*, Karl-Heinz Grosse Brinkhaus, and Thomas Esch

Institut für Organische Chemie und Biochemie der Universität Bonn,
Gerhard-Domagk-Str. 1, W-5300 Bonn 1, F.R.G.

Received May 27, 1991

Key Words: Triarylamines / Cation radicals / Electrochemistry / Redox catalysts / Voltammetry, cyclic

21 triarylamines (**1n–1z**, **1za**, **1zb**) and triarylamine analogs (**2a**, **2b**, **3a**, **3b**, **4a**, **4b**) with substituents in at least all three *p* positions and some of their cation-radical hexachloroantimonates have been synthesized. The electrochemical behavior has been studied by cyclic voltammetry. Most of the compounds show chemically and electrochemically reversible first oxidation waves in the formation of the cation radicals. With the exception of **4a** and **4b**, the second wave for the formation of the dication is chemically irreversible. The UV spectra of the triarylamine cation radicals have been obtained in the presence of a slight excess of $SbCl_5$. A good Hammett correlation between the first anodic potential of only *p*-substituted triarylamines and the σ/σ^+ values has been established. Some redox-catalytic properties of triarylamine cation radicals are described.

Triarylamine cation radicals are homogeneously reacting electrontransfer systems with oxidation potentials which can be varied over a wide range by proper selection of the *ortho* and *para* substituents[2,3]. Stable cation radicals are formed, if at least all *para* positions are blocked by substituents from immediate attack of nucleophiles[1–3]. Therefore, in numerous cases they have been applied as mild and selective oxidizing agents either in stoichiometric amounts as stable cation-radical salts or in catalytic amounts with electrochemical generation and in situ regeneration (indirect electrooxidations). Examples are deprotection of alcohols[4,5] and carboxylic acids[6] from their substituted benzyl ethers and esters, cleavage of carbon–sulfur bonds in dithioacetals[7], benzyl and *p*-methoxybenzyl thioethers[8], thiol esters[9], and *S*-glycosides[10], transformation of *o*-nitrophenylsulfenamides into the corresponding sulfenimines[11], side-chain oxidations of alkyl-substituted aromatic compounds[12,13], benzyl alcohol oxidations[14], α-methoxylations of aliphatic ethers and acetals[15], allylic oxidation of olefins[16], amine oxidations[17], α oxidations of ketones via their enols[18], oxidation of azomethine derivatives for the formation of N heterocycles[19], and disengagement of organic ligands from their iron carbonyl complexes[20]. Triarylamine cation radicals, however, are also suitable to induce cycloaddition and cycloreversion reactions via olefin cation radicals according to a mechanism which has been formulated as electron-transfer chain reactions. These include cation-radical Diels-Alder reactions[21], dioxetane[22] and endoperoxide[22,23] formations, and cycloreversion reactions[24].

A number of triarylamines and their cation-radical salts have been prepared previously. Among them are tris(4-methoxyphenyl)-amine (**1a**)[2,23,25–27], tri-*p*-tolylamine (**1b**)[2,23,25,26,28], tris(4-bromophenyl)amine (**1c**)[1,2,23,28,29,30], bis (4-bromophenyl) (2,4-dibromophenyl)amine (**1d**)[1], (4-bromophenyl)bis(2,4-dibromophenyl)amine (**1e**)[1], tris(2,4-dibromophenyl)amine (**1f**)[1,23,29,31], tris(4-acetylphenyl)amine (**1g**)[29], trimethyl triphenylamine-4,4′,4″-trisulfonate (**1h**)[29], tris(4-nitrophenyl)amine (**1i**)[32], tris(4-methoxycarbonylphenyl)amine (**1k**)[26], tris(4-chlorophenyl)amine (**1l**)[23,26], and tris(4-cyanophenyl)amine (**1m**)[33].

A prerequisite for the successful application of triarylamine cation radicals as redox catalysts is the availability of a large spectrum of triarylamines so that the properties of the catalyst, for example the oxidation potentials, can be matched to those of the substrate to be transformed. In addition, the stability of the cation radicals must be high so that the catalyst is not lost in side reactions, and a sufficient solubility must be ensured. Therefore, we have synthesized a large number of differently substituted triarylamines in addition to those already known in the literature[1,2] and have published some preliminary results[3,34]. In this paper we report on the synthesis, electrochemical, spectroscopical, and Hammett behavior, as well as redoxcatalytic properties in detail.

Syntheses of Substituted Triarylamines and their Cation Radical Hexachloroantimonates

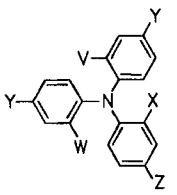
The following compounds containing triarylamine structures have been synthesized: substituted triphenylamines **1n–1zb**, *N*-phenylcarbazoles **2a**, **b**, *N*-phenylacridones **3a**, **b**, and tetraphenyl *p*-phenylenediamines **4a**, **b**.

a) New Triarylamine Derivatives Starting from Triphenylamine

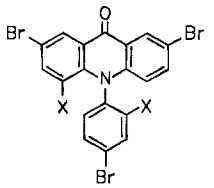
To obtain triarylamines with oxidation potentials between those of tris(4-bromophenyl)amine (**1c**) (E° = 1.3 V vs. NHE) and tris(2,4-dibromophenyl)amine (**1f**) (E° = 1.72 V vs. NHE)[1,2] triphenylamines containing four or five bromo substituents have been used (**1c**, **1d**)[1]. However, they have to be prepared by careful reaction with the appropriate amount of bromine. Therefore, we tried to brominate the known compounds tris(4-acetylphenyl)amine (**1g**) (E° = 1.5 V vs. NHE) or tris(4-cyanophenyl)amine (**1m**) (E° = 1.68 V vs. NHE). However, in the case of **1g** only side-chain

 © VCH Verlagsgesellschaft mbH, D-6940 Weinheim, 1991 0009–2940/91/1111–2557 $ 3.50+.25/0

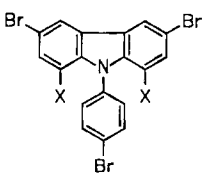
bromination occured, while **1m** was unreactive towards bromine in the presence of ferrum reductum. Therefore, we started from triphenylamine. By reaction with trifluoroacetic anhydride in trifluoroacetic acid we obtained diphenyl(4-trifluoroacetylphenyl)amine in 84%. Bromination with the appropriate amounts of bromine resulted in the formation of bis(4-bromophenyl)(4-trifluoroacetylphenyl)amine (**1n**) (88%, E° = 1.45 V vs. NHE) and bis(2,4-dibromophenyl)(2-bromo-4-trifluoroacetylphenyl)amine (**1o**) (97%, E° = 1.86 V vs. NHE), respectively. Wittig olefination of both compounds by triphenylphosphonium methylid resulted in the formation of bis(4-bromophenyl)[4-(1-trifluoromethylvinyl)phenyl]amine (**1p**) (75%, E° = 1.28 V vs. NHE) and bis(2,4-dibromophenyl)[2-bromo-4-(1-trifluoromethylvinyl)-phenyl]amine (**1q**) (71%, E° = 1.72 V vs. NHE). A strong influence on the oxidation potentials of triarylamines is excerted by nitro substituents[2]. Tris(4-nitrophenyl)amine (**1i**), although easy to prepare[32], is, however, only sparsely soluble in organic solvents so that the oxidation potential could only be determined in the presence of nitrobenzene (E° = 1.8 V vs. NHE). Bromination of bis(4-nitrophenyl)phenylamine[2] afforded (4-bromophenyl)[bis(4-nitrophenyl)]amine (**1r**) (93%, E° = 1.64 V vs. NHE) with a somewhat higher solubility.



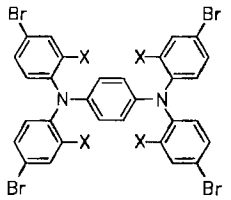
	V	W	X	Y	Z
1a	H	H	H	OCH_3	OCH_3
1b	H	H	H	CH_3	CH_3
1c	H	H	H	Br	Br
1d	H	H	Br	Br	Br
1e	H	Br	Br	Br	Br
1f	Br	Br	Br	Br	Br
1g	H	H	H	$COCH_3$	$COCH_3$
1h	H	H	H	SO_2OCH_3	SO_2OCH_3
1i	H	H	H	NO_2	NO_2
1k	H	H	H	$COOCH_3$	$COOCH_3$
1l	H	H	H	Cl	Cl
1m	H	H	H	CN	CN
1n	H	H	H	Br	$COCF_3$
1o	Br	Br	Br	Br	$COCF_3$
1p	H	H	H	Br	$C(CF_3)=CH_2$
1q	Br	Br	Br	Br	$C(CF_3)=CH_2$
1r	H	H	H	NO_2	Br
1s	H	H	H	Li	Li
1t	H	H	H	$Si(CH_3)_3$	$Si(CH_3)_3$
1u	H	H	H	$COCF_3$	$COCF_3$
1v	H	H	H	COOH	COOH
1w	H	H	COOH	Br	Br
1x	Br	Br	COOH	Br	Br
1y	H	H	$COOCH_3$	Br	Br
1z	H	H	$COOCH_2(4\text{-}NO_2)Ph$	Br	Br
1za	H	H	H	CF_3	CF_3
1zb	H	H	H	C_2F_5	C_2F_5



2a X = H
2b X = Br



3a X = H
3b X = Br

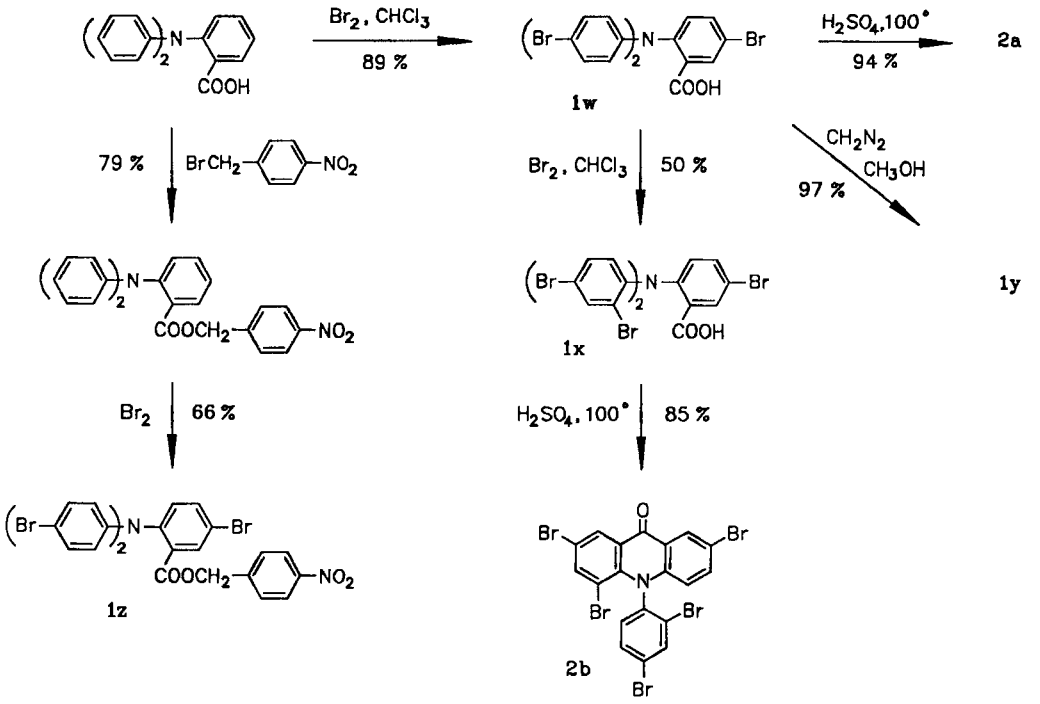


4a X = H
4b X = Br

b) Triarylamine Derivatives via Tris(4-lithiophenyl)amine (1s) Starting from Tris(4-bromophenyl)amine (1c)

The synthesis of *para*-substituted triarylamines is possible by starting from triphenylamine which is either subjected to the reaction with electrophiles[29] (see above) or to the Ullmann reaction. However, the latter one requires drastic reaction conditions, the separation of the products is tedious, and the yields are low[35]. A third possibility is the formation of tris(4-lithiophenyl)amine (**1s**) followed by quenching with electrophiles. Lithiation of triphenylamine leads only to monometalation in the *meta* position. Starting from tris(4-bromophenyl)amine (**1c**), the lithiation with *n*-butyllitium in benzene gave only unsatisfactory results[29]. We found[49] that the reaction of **1c** in diethyl ether with 3 equivalents of *n*BuLi (1.6 M in hexane) took only several minutes. A white precipitate was formed which dissolved when the electrophile was added. This procedure was especially effective when methyl iodide was used as electrophile; **1b** was obtained in 89% yield, while the usual Ullmann reaction gave only 11%[29]. With trimethylsilyl chloride tris(4-trimethylsilylphenyl)amine (**1t**) was formed in 78%. Even tris(4-trifluoroacetylphenyl)amine (**1u**) was obtained in 24% yield, while trifluoroacetylation of triphenylamine only gave the monosubstituted product (see above). Surprisingly, the reaction of **1s** failed with ethyl iodide or ethyl tosylate. The reaction of **1s** with iodine afforded tris(4-iodophenyl)amine (74%). The same product was obtained with pentafluoroethyl iodide in 84% yield obviously by halogen-metal exchange between **1s** and the electrophile. Carboxylation of **1s** was also possible in a strong CO_2 stream at 0°C in an ultrasonic bath. The crude product (90%) was purified by liquid chromatography on reversed phase column material giving 29% of 4,4′,4″-nitrilotrisbenzoic acid (**1v**)[36]. Starting from **1v**, a number of macrobicyclic hexalactones bearing two triphenylamine units as trifunctional spacers could be synthesized and their host-guest and electrochemical properties studied[36]. Also, tris(4-methoxyphenyl)amine (**1a**)

Scheme 1



could be obtained by the reaction of **1s** with nitrobenzene in dry diethyl ether under nitrogen at −100°C followed by methylation with dimethyl sulfate. The nitrobenzene acts as oxygen transfer agent for **1s** with the formation of tris(4-hydroxyphenyl)amine analogous to the reaction of nitrobenzene with phenyllithium reported by Köbrich[37]. **1a** may, however, be easier prepared by exchange of the bromine substituents in **1c** by methanol upon $Cu^{(I)}$ catalysis[27].

c) Triarylamine Derivatives of *N,N*-Diphenyl-2-aminobenzoic Acid

N,N-Diphenyl-2-aminobenzoic acid itself is not converted into stable cation radicals. Because of the free *para* positions, the cation radicals undergo the usual coupling to give the benzidine system. However, stable triarylamine redox systems can be obtained by starting from this compound according to Scheme 1. In this manner the triarylamines **1w**, **1x**, **1y**, and **1z** and the brominated acridones **2a**, **2b**, which may be seen as bridged triarylamines, could be obtained.

d) Formation of Perfluoroalkyl Triphenylamines

Substituents with a strong electronic effect are perfluoroalkyl groups like CF_3 and C_2F_5 which have been described to be stable and to improve solubility. Therefore, perfluoroalkyl-substituted triarylamines should have a very positive oxidation potential but at the same time a high stability and good solubility.

The synthesis of tris[4-(trifluoromethyl)phenyl]amine (**1za**) starting from 4-(trifluoromethyl)acetanilide and 1-bromo-4-(trifluoromethyl)benzene was performed under the conditions of an Ullmann reaction followed by alkaline hydrolysis; **1za** was isolated in only 4% yield together with bis(4-trifluoromethylphenyl)amine (22%). Tris(4-pentafluoroethylphenyl)amine (**1zb**) could be synthesized by a copper-catalyzed reaction between **1c** and pentafluoroethyl iodide in DMF at 80−140°C in a bomb tube. Because many by-products were formed, the isolation was difficult, giving only 22% of **1zb**.

e) Formation of Substituted *N*-Phenylcarbazoles

Similar to the acridones **2a**, **2b**, *N*-phenylcarbazoles are a bridged type of triarylamines. Stable redox systems can be expected to result from the brominated derivatives. 3,6-Dibromo-9-(4′-bromophenyl)carbazole (**3a**) was already described previously[1]. Further bromination of **3a** gave only mixtures of compounds. Therefore, in this case the Ullmann reaction between 1,3,6,8-tetrabromocarbazole and 1-bromo-4-iodobenzene was performed to give 1,3,6,8-tetrabromo-9-(4′-bromophenyl)carbazole (**3b**) which was contaminated with equal amounts of the 9-(4′-iodophenyl) derivative.

f) Formation of Substituted Tetraphenyl-*p*-phenylenediamines

Stable cation radicals of the triarylamine type could also be obtained by bromination of tetraphenyl-*p*-phenylenediamines. Thus, bromination with four equivalents of bromine in chloroform results in the formation of *N,N,N′,N′*-tetrakis(4-bromophenyl)-*p*-phenylenediamine (**4a**, 56%) while treatment with 8 equivalents of bromine yields *N,N,N′,N′*-tetrakis(2,4-dibromophenyl)-*p*-phenylenediamine (**4b**, 45%).

g) Synthesis of the Hexachloroantimonate Cation-Radical Salts

The hexachloroantimonate cation-radical salts of triarylamines are usually easy to prepare by the addition of a solution of $SbCl_5$ in dichloromethane to a solution of the triarylamine in the same solvent[1,30]. After pouring the mix-

ture into pentane, the cation-radical salts precipitate and can be isolated by filtration (Table 1).

Table 1. Yields of the triarylaminiumyl hexachloroantimonates

Triarylamine	Triarylamine Cation Radical Salt	Yield [%]
1i	**1i**$^{\bullet+}SbCl_6^-$	82[a]
1n	**1n**$^{\bullet+}SbCl_6^-$	70
1o	**1o**$^{\bullet+}SbCl_6^-$	75
1y	**1y**$^{\bullet+}SbCl_6^-$	90[b]
1z	**1z**$^{\bullet+}SbCl_6^-$	71
1za	**1za**$^{\bullet+}SbCl_6^-$	92[b]
3a	**3a**$^{\bullet+}SbCl_6^-$	93

[a] In the presence of air only stable for several minutes. — [b] Partial hydrolysis.

The ester group in **1y** and the CF_3 group in **1za** are partially hydrolyzed under the reaction conditions. The cation radical of **1i** is oxidizing the water in moist air because of its highly positive oxidation potential; **2a** and **2b** do not form cation radical salts upon treatment with $SbCl_5$. The reaction only results in the formation of a crystalline addition product. Attempts to prepare the cation radical salt of **3b** failed due to its instability in the medium used.

Electrochemical and Spectroscopic Properties of Substituted Triarylamines and Related Compounds

Electroanalytical data have been obtained by cyclic voltammetry in acetonitrile using either a platinum or a glassy carbon-disc anode together with an $Ag/AgNO_3$ (0.1 M in CH_3CN) reference electrode. The potentials have been recalculated vs. a normal hydrogen electrode (NHE) by calibration of the reference electrode with an Ag/AgCl electrode. For the reversible or quasireversible systems with i_{pc}/i_{pa} values being larger than 0.85, the first oxidation potential is determined as the formal standard potential, E°, and corresponds to the potential at 85.2% of the peak current of the first anodic peak[38] (Table 2).

Most of the triarylamines listed in Table 2 show chemically (peak current ratio $i_{pc}/i_{pa} = 1$)[39] and electrochemically ($\Delta E_p \approx 60$ mV) reversible first oxidation waves in the formation of the cation radicals. In the case of **3b**, ΔE_p is slightly larger because this compound is contaminated with the 4′-iodo derivative which should have a slightly different redox potential. The second wave leading to the dication in most cases is chemically irreversible indicating the high reactivity of these species. Only in the case of the brominated *p*-phenylenediamines **4a** and **4b** in dichloromethane also the second wave is electrochemically and chemically reversible, if measured in dichloromethane. The peak current ratio for the second wave is only slightly smaller than 1 up to a potential scan rate of 200 mV/s (Figure 1).

When a platinum anode in acetonitrile is used, **4a** shows only one sharp and strong oxidation peak at 1.26 V, typical of the adsorption of the starting material, accompanied by

Table 2. Electroanalytical data of triarylamines and related compounds in acetonitrile

Comp.	E°_1[a] [V]	E_p[b] [mV]	i_{pc}/i_{pa}[c]	$i_{pa}/\sqrt{v}$	E_2[d] [V]
1i[e]	1.8	85	0.85	const.	
1n	1.45	60	0.99	const.	
1o	1.85	61	0.85	const.	
1p	1.28	60	0.94	const.	1.98
1q	1.72	62	0.89	const.	
1r	1.64	80	0.89	const.	2.2
1t	1.08	60	0.93	const.	
1u	1.68	65	0.94	const.	
1w	1.41	60	1	const.	2.13
1x	1.75[g]	--	--	const.	
1y	1.42	70	0.98	const.	2.1
1z	1.39	62	0.98	const.	2.2
1za	1.60	65	0.99	const.	
1zb	1.64	60	0.98	const.	
2a	1.85	70	0.98	const.	2.4
2b	2.04[g]	--	--	const.	
3a	1.68	62	0.93	const.	
3b	1.83	75	0.93	const.	
4a[f]	0.90	60	1	const.	1.26
4b[f]	0.93	60	1	const.	1.31

[a] Formal standard potential. — [b] Separation of anodic and cathodic peak of the first wave, extrapolated to a potential scan rate $v = 0$ mV/s. — [c] Ratio of anodic and cathodic peak current of the first wave measured at potential scan rates of 49 or 81 mV/s. — [d] Anodic peak potential of the second wave. — [e] In the presence of nitrobenzene as cosolvent. — [f] In dichloromethane. — [g] Anodic peak potential.

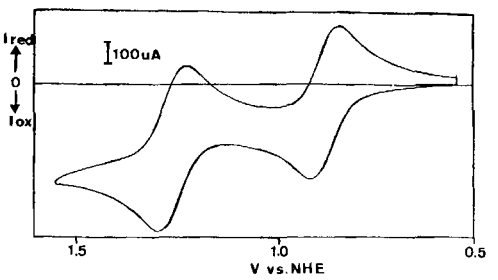


Figure 1. Cyclovoltammogram of **4a** in CH_2Cl_2/Bu_4NClO_4 (0.2 M) at 40 mV/s at a Pt electrode

the usual two one-electron reduction waves. In all cases, the anodic peak current of the first wave depends linearly on the square root of the potential scan rate ($i_{pox}/\sqrt{v}$ = constant), indicating a diffusion-controlled process. In cases in which the peak current ratio for the first wave is 0.94 or less, the cation radicals are chemically unstable and undergo slow follow-up reactions. In the case of **1x** and **2b** the cation radicals are very unstable so that no values for the peak potential difference and the peak current ratio can be obtained. The cation radical of **2b** has such a high oxidation potential that electron transfer from the electrolyte is possible. If the measurements of compounds **1n** and **1o** are performed in the presence of methanol, a new reversible redox pair appears at 150 mV (**1n**) and 120 mV (**1o**), respectively (Figure 2).

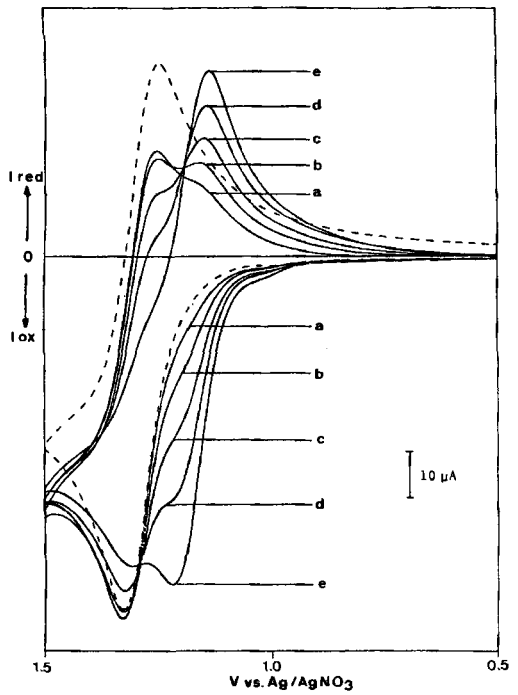


Figure 2. Cyclovoltammogram of **1o** in the absence and in the presence of methanol at 90 mV/s at a Pt electrode; broken line: **1o** (1×10^{-3} M) in $CH_3CN/LiClO_4$ (0.1 M); solid line: **1o** (1×10^{-3} M) in CH_3CN/CH_3OH (5:1)/$LiClO_4$ (0.1 M); a: scan no. 1; b: scan no. 5; c: scan no. 10; d: scan no. 20; e: scan no. 40

The anodic and cathodic peaks of this redox pair increase with the number of scans until the original pair is totally removed. The addition of a drop of sulfuric acid results in the total regeneration of the original picture. When trying to isolate the new redox system by chromatography on silica gel only the original starting material is obtained. We conclude that the carbonyl groups undergo acetalization with methanol under the catalytic influence of the protons produced at the anode.

1t$^{\bullet+}$ is not totally stable under the conditions of the voltammetric measurements. If used as mediator for the indirect anodic oxidation of a sulfenamide, **1t** is totally desilylated to triphenylamine.

Table 3. Long-wavelength absorbance maxima of triarylamine cation radicals in acetonitrile

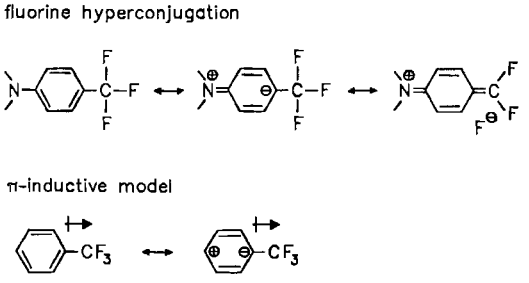
Comp.	λ_{max} [nm]	Comp.	λ_{max} [nm]
1b$^{\bullet+}$	668	**1i**$^{\bullet+}$	622
1n$^{\bullet+}$	726	**1r**$^{\bullet+}$	712
1t$^{\bullet+}$	694[a]	**1u**$^{\bullet+}$	674
1w$^{\bullet+}$	736	**1y**$^{\bullet+}$	736
1z$^{\bullet+}$	742	**1za**$^{\bullet+}$	622
1zb$^{\bullet+}$	628	**3a**$^{\bullet+}$	820

[a] Presumably cation radical of the tetraphenylbenzidine.

The longest wavelength UV/Vis absorbance maxima of the cation radicals have been obtained by measurement of the triarylamine in acetonitrile in the presence of a small excess of $SbCl_5$ (Table 3).

The spectral behavior of other substituted triarylamine cation radicals has been reported[1,40–42]. Walter[40] and Neugebauer[41] have shown that the longest wavelength absorption maximum in the UV/Vis spectrum of the triphenylamine cation radical always undergoes a bathochromic shift by both electron-donating and electron-withdrawing *p* substituents, the only uncommented exception being the fluoro substituent. This is due to the extension of the π system by both types of substituents. This tendency has been supported by Neugebauer[41] who has shown that the ESR coupling constant α(N) is lowered by both types of substituents. With the exception of **1i**$^{\bullet+}$, **1za**$^{\bullet+}$, and **1zb**$^{\bullet+}$, the values given in Table 3 are in accordance with the findings mentioned above, as they are larger than the longest wavelength maximum of the cation radical of triphenyl amine (λ_{max} = 650 nm[43]). The different behavior of the perfluoroalkyl-substituted triarylamines **1za** and **1zb** can be understood, if one assumes a socalled π-inductive effect introduced by Holtz[44] instead of "fluorine hyperconjugation" to account for the reactivity of perfluoroalkyl substituents (Scheme 2).

Scheme 2



Fluorine hyperconjugation should extend the π system also in the case of **1za**$^{\bullet+}$ and **1zb**$^{\bullet+}$ and result in a bathochromic shift. Instead, the π-inductive effect leads to a decrease of the polarization of the π system and thus to the observed hypsochromic shift. A similar behavior has been observed in the case of perfluoroalkylanilinium compounds[44]. In agreement with this model is also the fact that for Hammett plots the ordinary σ constants can be used.

The electronic effects of the substituents in triarylamine cation radicals on the oxidation potentials can only be studied systematically, if only *p* substituents are present; *o* and *m* substituents show additional steric effects. In the case of the bromo-substituted triphenylamines the electronic and steric effects of the *o* and *p* substituents can be discriminated by voltammetric studies. In addition, a linear relationship between the redox potentials of these amines and the long-wavelength UV/Vis absorbance maxima of the cation radicals is observed[1]. In the case of macrobicyclic host molecules bearing triphenylamine units as trifunctional spacers the influence of steric hindrance and strain on the redox potentials has been demonstrated[36]. A correlation of the long-wavelength absorbance maxima of a large variety of *p*-substituted triarylamines with the Hammett σ constants has not been found. This has been characterized by Walter[39] as "non-Hammett behaviour". A correlation cannot be es-

tablished either between the long-wavelength absorbance maxima and the redox potentials of the triarylamine cation radicals. Such a correlation cannot be expected because σ constants and redox potentials are mainly influenced by electronic effects, and in the case of oxidations these parameters depend on the absolute energy of the HOMOs. The longwavelength absorbance maxima of the cation radicals, as has been shown above, depend on the extension of the π system, which determines the energy difference between the HOMOs and LUMOs. A very good linear relationship is, however, obtained, if the redox potentials of the *p*-substituted triarylamines are correlated with the σ_p or σ_p^+ values (for electron-donating groups σ_p^+ values have to be used). To obtain a value for the reaction constant, ϱ, the redox potentials have to be converted into a ratio of equilibrium constants. This has been done by using the following equation derived from the Nernst equation.

$$\lg \frac{K}{K^\circ} = \frac{1}{0.059} \cdot (E^\circ - E)[\mathrm{V}] = \sigma \cdot \varrho$$

Triphenylamine with $E^\circ = 1.17$ V was used as standard. In this way (including the values for the NMe_2 substituent not shown in Figure 3: $\lg K/K^\circ = 17$; $\sigma_p^+ = -1.7$) a value of −10.98 with a correlation coefficient of 0.992 was obtained for ϱ (Figure 3).

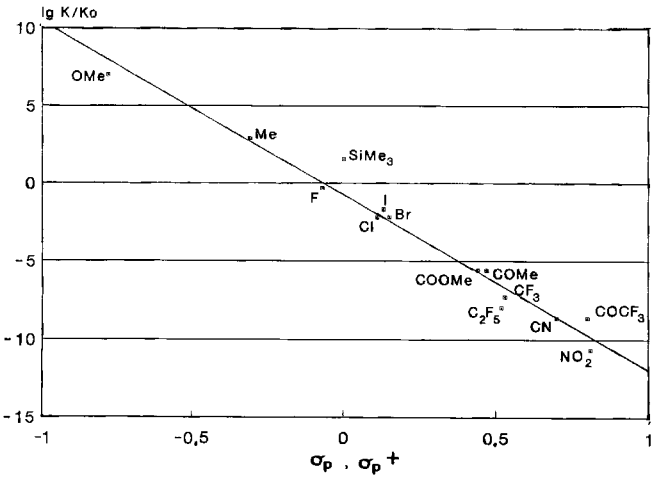


Figure 3. Hammett correlation between $\lg K/K^\circ$ (represented by $1/59\ (E^\circ - E)$ [mV]) and σ_p or σ_p^+ values for only *p*-substituted triarylamines (*p* substituents are indicated in the diagram) by using triphenylamine ($E^\circ = 1.17$ V) as a standard

The high negative value of ϱ demonstrates the high sensitivity of the cation radicals towards the electronic effects of the *p* substituents. This correlation can be used to predict the oxidation potentials of tri-*p*-substituted triarylamines; σ and σ^+ values were taken from the literature[45].

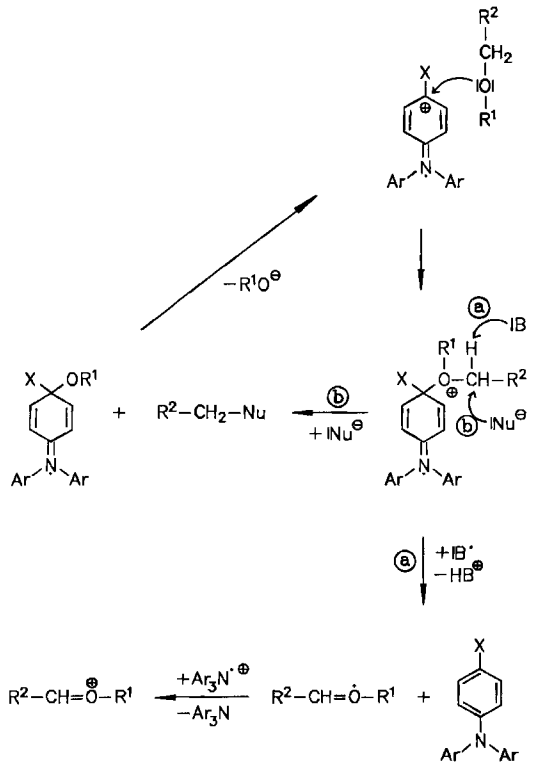
Redox-Catalytic Behavior of Triarylamin Cation Radicals

As we have shown earlier, electrogenerated triarylamine cation radicals can be used effectively as regenerable redox catalysts (indirect electrolysis)[3]. In this type of rection, the triarylamine redox pair acts as homogeneous catalyst for the transfer of the electrons from the substrate to the electrode. The stability of the triarylamine cation radicals in redox-catalytic reactions strongly depends on their substitution pattern, the reaction medium, and also on the overall rate of the catalytic reaction. If the catalytic cycle is slow, higher stationary concentrations of the cation radicals favor side reactions. For example 4-bromo- and 4-iodo-substituted cation radicals can undergo 4,4′ coupling with loss of the halo substituents leading to the benzidine cation radical and dication, respectively[46]. This type of debromo dimerization has been observed with tris(4-bromophenyl)ammoniumyl (**1c**) in acetonitrile at 0°C[47]. Similarly, tris(2,4-dibromophenyl)amine (**1f**) undergoes successive slow replacement of the *p*-bromo by *p*-chloro substituents if it is oxidized in methanol/dichloromethane in an undivided cell. This reaction may proceed as a nucleophilic *ipso* substitution in the *para* position of the cation radical[48] in which the cathodically formed Cl^- (by reduction of CH_2Cl_2) acts as the nucleophile. In methanol the radical cations of **1f** can undergo *several thousand turnovers without considerable loss of material* as shown in the indirect electrochemical side-chain oxidation of alkyl-substituted aromatics[12]. This is different in the case of **1c** which has been found to form (4-bromo-2-methoxyphenyl)bis(4-bromophenyl)amine by anodic nuclear substitution if used in pure methanol[49]. In the presence of acetate the corresponding acetoxy compound has been isolated[47].

If triarylamines are used as redox catalysts, the mechanism of the homogeneous redox reaction needs not always be an outer-sphere electron transfer. While in some cases the simple electron transfer is undisputed, for example in the reaction of $\mathbf{2c}^{\bullet+}$ with dithioacetals, thioethers[7,8], *o*-nitrophenylsulfenamides[11], bromide or iodide ions[50], in other cases an inner-sphere electron transfer via an intermediate complex is more likely. One obvious reason for the different behavior is the fact that in some redox-catalytic applications of electrogenerated triarylamine cation radicals the potential difference [$E^\circ(Ar_3N)$ − E(substrate)] is more negative than −1 V. This is the case in the redox-catalytic oxidation of alkyl-substituted aromatics[12] or aliphatic ethers and acetals[15]. The observed rates are higher than those which would be expected for an outer-sphere electron transfer. The assumption of an interaction between triarylamine cation radicals and some nucleophilic substrates is underlined by the fact that triarylamine cation radicals clearly show Lewis acid activity in addition to their redox properties. For example, if the reaction between $\mathbf{1f}^{\bullet+}$ and 4-methoxybenzyl *n*-decanoate is performed in the presence of anisol, besides decanoic acid and 4-methoxybenzaldehyde also dianisylmethane and 4-methoxybenzyl alcohol are formed in changing amounts. The dianisylmethane is clearly a product of the reaction between anisol and the 4-methoxybenzyl cation generated by the Lewis acid activity of $\mathbf{1f}^{\bullet+}$. In addition, the cleavage of benzhydryl esters needs less than stoichiometric amounts of $\mathbf{1f}^{\bullet+}$ $SbCl_6^-$. These observations may be explained by a common picture in which a complex (with or without bond formation) between the electrophilic $Ar_3N^{\bullet+}$ and the nucleophilic substrate suc-

cessively undergoes parallel reactions by Lewis acid activation or redox activation (Scheme 3).

Scheme 3. Proposed mechanism for the action of triarylamine cation radicals as redox catalysts (path a: innersphere electron transfer) or Lewis acid catalysts (path b)



A similar inner-sphere electron-transfer behavior has recently been postulated by Eberson for the Diels-Alder dimerization of 1,3-cyclohexadiene, catalyzed by $\mathbf{1c}^{\cdot+}$ $SbCl_6^-$, in which the triarylamine cation radical may play the role of an electrophile and at the same time provide the driving force for the reaction by its oxidative power[51].

Some of the new triarylamine compounds have been used effectively in indirect anodic oxidations. For example, **3a** has been applied as mediator in the electrooxidation of benzylic alcohols[48], **1r** was effective in the indirect anodic cleavage of benzyl esters[49], and **4a** worked very well in the selective deblocking of a 3,4-dimethoxybenzyl ether group in the presence of a 4-methoxybenzyl ether function[63].

Fruitful discussions with *L. Eberson*, Lund, have helped to clarify the redox behavior of triarylamine cation radicals. Financial support by the *Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie*, and the *BASF Aktiengesellschaft* is gratefully acknowledged.

Experimental

^{1}H NMR: Varian EM 360, Bruker WH-90, Bruker WM 300 (δ values, TMS internal standard). – ^{13}C NMR: Bruker WH-90 (δ values, TMS internal standard). – IR: Pye-Unicam SP 1100. – UV-Vis: CARY 219 (Varian); Perkin-Elmer spectrometer 550. – MS: A.E.I. MS-9, MS-30, and MS-50. – Melting points (uncorrected): Kofler micro heating plate (Reichert). – Microanalyses: Perkin-Elmer CH-analyzer 240 and Heraeus CHNO-Rapid. – TLC analyses: TLC aluminum sheets, silica gel 60 F_{254} (Merck, Riedel-de Haën). – Preperative LC separations: Silica gel for flash chromatography 30–60 μm (Baker). – Preparative HPLC separations: Steel column, 16 mm, 0.5 m, LiChrosorb Si 60 (Merck), 7 μm. – Gas chromatographic analyses: Glass column, 2.2 mm, 2 m, 1% OV 101 on Chromosorb W (column 1) or glass column, 2 mm, 1.7 m, 1% OV 101 on Chromosorb WAWDCMS (column 2) in combination with Varian gas chromatograph 2740 or gas-chromatograph Fractovap 4100 (Carlo Erba).

Cyclohexane, petroleum ether, chloroform, diethyl ether, and carbon tetrachloride were purified by distillation. Methanol (Merck; p.a.; stored over molecular sieves, 4 Å), ethanol (Merck; p.a.), acetonitrile (Merck, Aldrich; p.a.), dichloromethane (Baker; p.a.), and the starting materials for synthesis (GC control for purity) were used as obtained.

Cyclic Voltammetry: Cyclic voltammograms were obtained by using a Wenking potentiostat PCA 72 L (Bank Elektronik, Göttingen) in combination with a Wavetek model 133 function generator or a Wenking potentioscan POS 73 with integrated function generator. The current-voltage curves were recorded with a Hewlett-Packard XY recorder, model 7045 A or 7044 A. As electrolysis cell a thermostated type EA 876-5 and 876-20 (Metrohm, Herisau) was used. The rotating-disc electrode, model 628-10 (Metrohm, Herisau), with Pt or glassy carbon tip (diameter 0.3 cm) was applied as stationary anode together with a Pt wire (diameter 0.5 mm) as cathode and an $Ag/AgNO_3$ (0.1 M in CH_3CN) reference electrode.

Diphenyl(4-trifluoroacetylphenyl)amine: To a solution of 24.5 g (100 mmol) of triphenylamine in 200 ml of CCl_4 a mixture of 63.0 g (300 mmol) of trifluoroacetic anhydride and 11.4 g (100 mmol) of trifluoroacetic acid was slowly added dropwise. After heating to reflux for 10 h, the reaction mixture was neutralized with a Na_2CO_3 solution (10% in water). The aqueous phase was separated and extracted four times with dichloromethane. The united organic extracts were washed twice with water, dried, and the solvent was evaporated. The crude product (34.6 g) was recrystallized from dichloromethane/cyclohexane to yield 28.7 g (84%), m.p. 86°C. – IR (KBr): $\tilde{\nu}$ = 1705 cm^{-1} (CO), 1590 (C=C), 1490 (C=C), 1340, 1180, 940, 860, 755, 695. – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 6.90–7.98 (AA'BB', 4H, C_6H_4), 7.10–7.55 (m, 10H, C_6H_5). – MS (70 eV): *m/z* (%) = 341 (100) [M^+], 272 (85), 244 (22), 243 (18), 242 (15), 241 (12).

$C_{20}H_{14}F_3NO$ (M^+) Calcd. 341.1028 Found 341.1025 (MS)

Bis(4-bromophenyl)[4-(trifluoroacetyl)phenyl]amine (**1n**): To a solution of 6.8 g (20 mmol) of diphenyl[4-(trifluoroactyl)phenyl]-amine in 70 ml of $CHCl_3$, 6.3 g (40 mmol) of bromine in 20 ml of $CHCl_3$ was slowly added at room temp. After HBr evolution had ceased, the solution was washed with 20 ml of water, 20 ml of 2 N NaOH, and again 20 ml of water. The organic phase was dried and the solvent evaporated. The crude product (9.7 g) was recrystallized from dichloromethane/cyclohexane to yield 8.8 g (88%), m.p. 126°C. – IR (KBr): $\tilde{\nu}$ = 1700 cm^{-1} (CO), 1600 (C=C), 1580 (C=C), 1485 (C=C), 1320, 1170, 1145, 930, 820. – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 6.90–7.04 and 7.83–8.02 (AA'BB', 4H, C_6H_4), 7.13–7.28 and 7.58–7.73 (AA'BB', 8H, C_6H_4). – MS (70 eV): *m/z* (%) = 501, 499, 497 (49, 100, 51) [M^+], 432, 430, 428 (29, 60, 30), 404, 402, 400 (3, 6, 3), 323, 321 (18, 20), 322, 320 (16, 14), 242 (17), 241 (35).

$C_{20}H_{12}Br_2F_3NO$ (M^+) Calcd. 500.9196, 498.9215, 496.9237
Found 500.9190, 498.9195, 496.9270 (MS)

[2-Bromo-4-(trifluoroacetyl)phenyl]bis(2,4-dibromophenyl)-amine (**1o**): To a solution of 8.52 g (25.0 mmol) of di(phenyl[(4-

(trifluoroacetyl)phenyl]amine in 100 ml of $CHCl_3$, 24.0 g (150 mmol) of bromine was slowly added. The reaction mixture was heated to reflux until total conversion was achieved (GC control on column 1). After 6 d, the workup was performed as in the case of **1n**. The crude product (19 g) was filtered through silica gel by using dichloromethane/cyclohexane as eluent, m.p. 83–85°C. – IR (KBr): $\tilde{\nu}$ = 1722 cm^{-1} (CO), 1599 (C=C), 1580 (C=C), 1496 (C=C), 1471 (C=C), 1310, 1215, 1190, 1156, 1056, 1048, 980, 968, 880, 825, 770. – ^1H NMR (90 MHz, $CDCl_3$): δ = 6.75 (d, J = 8.5 Hz, 2H), 6.89 (d, J = 8.5 Hz, 1H), 7.40 (dd, J = 8.5 and 2 Hz, 2H), 7.80 (d, J = 2 Hz, 2H), 7.92 (dm, J = 8.5 Hz, 1H), 8.30 (m, 1H). – MS (70 eV): m/z (%) = 741, 739, 737, 735, 733, 731 (11, 49, 89, 100, 50, 9) [M^+], 672, 670, 668, 666, 664, 662 (0.7, 7.5, 15, 16, 7.5, 0.7), 579, 577, 575, 573 (4.4, 12.5, 13, 4.2), 563, 561, 559, 557, 555 (0.5, 2.3, 4.5, 2.5, 0.5), 510, 508, 506, 504 (3.6, 10.2, 10, 3.6), 482, 480, 478, 476 (1.6, 4.0, 4.1, 1.6), 401, 399, 397 (6.3, 13, 6.2), 320, 318 (5.9, 5.9), 239 (15).

Bis(4-bromophenyl)[4-(1-trifluoromethylvinyl)phenyl]amine (**1p**): According to a literature procedure[52], 2.3 mmol of *n*-butyllithium was added to a solution of 890 mg (2.5 mmol) of methyltriphenylphosphonium bromide in absolute diethyl ether (100 ml) under nitrogen. After 30 min, 998 mg (2.0 mmol) of **1n**, dissolved in 20 ml of absolute diethyl ether, was added to the orange-yellow solution. After 1 h, the precipitate was removed by filtration and washed with ether. From the collected ether solutions, the solvent was evaporated and the residue purified twice by HPLC using dichloromethane/cyclohexane mixtures first in ratios of 2:1 then in ratio of 1:12 as aluents. Besides 650 mg (65%) of **1p** (oil), 135 mg (14%) of **1n** was recovered. – IR (NaCl): $\tilde{\nu}$ = 1615 cm^{-1} (C=C), 1590 (C=C), 1510 (C=C), 1490 (C=C), 1315, 1290, 1205, 1180, 1135, 1015, 847, 830. – ^1H NMR (90 MHz, $CDCl_3$): δ = 5.75 (q, J_{HF} = 1.4 Hz, 1H), 5.90 (q, J_{HF} = 1.8 Hz, 1H), 6.90–7.50 (2 × AA'BB', 12H, C_6H_3). – MS (70 eV): m/z (%) = 499, 497, 495 (50, 100, 50) [M^+], no other signal with more than 9%.

$C_{21}H_{14}Br_2F_3N$ (M^+) Calcd. 498.9405, 496.9424, 494.9443
Found 498.9431, 496.9443, 494.9427 (MS)

[2-Bromo-4-(trifluoromethylvinyl)phenyl]bis(2,4-dibromophenyl)amine (**1q**): **1q** was synthesized by analogy with **1p** by using 1.79 g (5.0 mmol) of methyltriphenylphosphonium bromide, 4.6 mmol of *n*-butyllithium, and 2.94 g (4.0 mmol) of **1o**. Besides 1.99 g (68%) of **1q**, 0.14 g (4.6%) of **1o** was recovered. – IR (NaCl): $\tilde{\nu}$ = 1605 cm^{-1} (C=C), 1500 (C=C), 1470 (C=C), 1305, 1185, 1135, 1090, 1055, 915, 880, 835, 820, 740. – ^1H NMR (90 MHz, $CDCl_3$): δ = 5.84 (q, J_{HF} = 1.4 Hz, 1H), 6.00 (q, J_{HF} = 1.8 Hz, 1H), 6.75 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 8.5 Hz, 1H), 7.30–7.50 (ddm, J = 8.5 and 2 Hz, 3H), 7.74 (d, J = 2 Hz, 1H), 7.79 (d, J = 2 Hz, 2H). – MS (70 eV): m/z (%) = 739, 737, 735, 733, 731, 729 (12, 52, 100, 99, 50, 9) [M^+], 577, 575, 573, 571 (28, 79, 80, 28), 415, 413 (15, 15), 346, 344 (7.5, 7.5), 265 (35), 264 (12), 239 (5), 238 (3).

(4-Bromophenyl)bis(4-nitrophenyl)amine (**1r**): To a solution of 2.3 g (7 mmol) of bis(4-nitrophenyl)phenylamine in 10 ml of $CHCl_3$, 1.1 g (7 mmol) of bromine was added at room temp. After stirring the orange-yellow solution for 7 d, the reaction mixture was filtered. The filtrate was treated with ethanol, thereby the crude product precipitated. The solid was recrystallized from $CHCl_3/C_2H_5OH$ to yield 2.7 g (93%) of **1r**, m.p. 318–321°C (sublimation starting at 258°C). – IR (KBr): $\tilde{\nu}$ = 1595 cm^{-1}, 1502, 1500 (aromat. CH), 1485 (C–N), 1577, 1335, 1310, 1270 (NO_2), 850. – ^1H NMR (300 MHz, $CDCl_3$): δ = 8.18–8.15 and 7.17–7.14 (AA'BB', 8H, $C_6H_4NO_2$), 7.57–7.55 and 7.08–7.06 (AA'BB', 4H, C_6H_4Br). – MS (70 eV): m/z (%) = 415, 413 (98, 100) [M^+], 399, 397 (1,1), 339, 337 (9,8), 323, 321 (19, 21), 322, 320 (14, 12), 288 (18), 242 (43), 241 (58). – UV ($CHCl_3$): λ_{max} (lg ε) = 410 nm, (4.42), 362 (4.23), 241 (4.16).

$C_{18}H_{12}BrN_3O_4$ (414.23) Calcd. C 52.19 H 2.92 N 10.14
Found C 51.84 H 2.92 N 10.18

General Procedure for the Formation of Triarylamine Derivatives via Tris(4-lithiophenyl)amine (**1s**) *Starting from Tris(4-bromophenyl)amine* (**1c**)

Tris(4-lithiophenyl)amine (**1s**): In a 100-ml three-necked flask, eqipped with argon inlet, septum, and reflux condenser with bubble gauge, 500 mg (1.03 mmol) of **1c** was dissolved in 30 ml of absolute diethyl ether under argon; 3.09 mmol of *n*-butyllithium (1.6 M in hexane) was added through a septum by using a syringe at room temp. After 20 s, the solution became turbid, and a white precipitate formed. A red or orange color was observed in some cases. After stirring at room temp. for 15 min, **1s** was treated with the electrophile without isolation. After the addition of a solution of the electrophile in diethyl ether by using a syringe, the white precipitate slowly dissolved, and the solution showed a yellow or green color. To complete the reaction, the mixture was heated to reflux for 2 h. Then the ether was evaporated, the residue dissolved in dichloromethane, the solution washed with water, dried with $MgSO_4$, and the solvent was evaporated. The resulting crude product was analyzed by gas chromatography (column 2). For the separation of dark byproducts, the material was filtered by using a short silica-gel column and dichloromethane/petroleum ether mixtures as eluents. Further purification was performed by recrystallization or column chromatography.

Tritolylamine (**1b**): According to the general procedure, 4.15 mmol of **1s** (from 4.15 mmol of **1c** and 12.4 mmol of *n*-butyllithium) was treated with 1.80 g (12.4 mmol) of CH_3I to give 1.05 g (89%) of **1b**. Melting point and other physical data were identical to literature values[26,53].

Tris[4-(trimethylsilyl)phenyl]amine (**1t**): According to the general procedure, 4.15 mmol of **1s** (from 4.15 mmol of **1c** and 12.4 mmol of *n*-butyllithium) was treated with 3.00 ml of trimethylsilyl chloride to give 1.49 g (78%) of **1t**, m.p. 210–212°C (after sublimation). – IR (KBr): $\tilde{\nu}$ = 2980 cm^{-1} (CH_3), 1590, 1570, 1505 (aromat. CH), 1330, 1285, 1265, 1250, 835, 730, 695. – ^1H NMR (90 MHz, $CDCl_3$): δ = 7.45–7.35 and 7.14–7.04 (AA'BB', 12H, C_6H_4), 0.25 (s, 27H, $SiCH_3$). – ^{13}C NMR (22.5 MHz, $CDCl_3$): δ = 148.11 (CN), 134.0 (CSi), 134.39 (CH), 123.55 (CH), –0.84 ($SiCH_3$). – MS (70 eV): m/z (%) = 463, 462, 461 (18, 42, 100) [M^+], 448, 447, 446 (9, 25, 55).

$C_{27}H_{39}NSi_3$ (461.89) Calcd. C 70.21 H 8.51 N 3.03
Found C 69.74 H 8.35 N 3.05

$C_{27}H_{39}NSi_3$ (M^+) Calcd. 461.2390 Found 461.2401 (MS)

Tris[4-(trifluoroacetyl)phenyl]amine (**1u**): According to the general procedure, 1.03 mmol of **1s** (from 1.03 mmol of **1c** and 3.09 mmol of *n*-butyllithium) was treated with 3.00 g (14.3 mmol) of trifluoroacetic anhydride to give a mixture of 9 compounds (gas chromatography, column 2). The crude product (500 mg) was heated to reflux in CCl_4. The residue (80.0 mg) and the first precipitate from the CCl_4 solution (55.0 mg) yielded 135 mg (24%) of **1u**, m.p. 200–212°C (yellow needles, from dichloromethane/petroleum ether). – IR (KBr): $\tilde{\nu}$ = 1720 cm^{-1} (CO), 1600, 1520 (aromat. CH), 1185 (CF). – ^1H NMR (90 MHz, [D_6]DMSO): δ = 8.15–8.05 and 7.33–7.24 (AA'BB', 12H, C_6H_4). – MS (70 eV): m/z (%) = 533 (47.2) [M^+], 464 (100), 436 (1), 367 (5), 339 (12), 242 (11), 197 (48).

$C_{24}H_{12}F_9NO_3$ (M^+) Calcd. 533.0588 Found 533.0631 (MS)

4,4',4''-Nitrilotrisbenzoic Acid (**1v**)[36]: According to the general procedure, 10.0 mmol of **1s** (from 10.0 mmol of **1c** and 33.6 mmol

of *n*-butyllithium) was treated in an ultrasonic bath with a CO_2 stream bubbling through the solution containing the precipitate for 30 min at 0°C followed by 30 min at room temp. Workup of the mixture with $NaHCO_3$ solution/ether after precipitation with HCl yielded 3.4 g of crude **1v**. Purification was achieved by chromatography on reversed-phase material (LiChroprep RP-8, 25–40 μm) with methanol/water (2.7:1) to give 1.1 g (29%) of **1v**, m.p. 271–272°C. – ^{1}H NMR (90 MHz, CD_3OD): δ = 7.21, 8.03 (AA'BB', 12H, C_6H_4). – MS (70 eV): *m/z* (%) = 337 (100) [M^+].

$C_{21}H_{15}NO_6$ (377.35) Calcd. C 66.84 H 4.01 N 3.71
Found C 66.84 H 4.17 N 3.95

Triarylamin Derivatives of 2-(Diphenylamino)benzoic Acid

2-[Bis(4-bromophenyl)amino]-5-bromobenzoic Acid (**1w**): To a solution of 4.86 g (16.9 mmol) of 2-(diphenylamino)benzoic acid in 200 ml of $CHCl_3$, 4.15 g (1.32 ml, 50.7 mmol) of bromine, dissolved in 50 ml of $CHCl_3$, was slowly added at room temp. After stirring for ca. 12 h, the major part of the solvent was evaporated and a layer of petroleum ether was put on top of the remaining organic phase. In the refrigerator, a dark green crystalline crude product precipitated which was washed several times with petroleum ether to yield light green crystals; yield 8.00 g (90%), m.p. 189 to 194°C. – IR (KBr): ν̃ = 3700–2400 cm^{-1} (CO_2H), 1700 (CO), 1585, 1490 (arom. CH). – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 1 Hz, 1H), 7.62 (dd, *J* = 9 Hz and 1 Hz, 1H), 7.06 (d, *J* = 9 Hz, 1H), 7.37–7.28 and 6.87–6.78 (AA'BB'). – MS (70 eV): *m/z* (%) = 529, 527, 525, 523 (33, 100, 100, 34) [M^+], 449, 447, 445 (2, 4, 2), 448, 446, 444 (4, 6, 4), 403, 401, 399 (11, 22, 11), 367, 365 (2, 2), 241 (10). – UV ($CHCl_3$): λ_{max} (lg ε) = 308 nm (3.6), 360 (4.41).

$C_{19}H_{12}Br_3NO_2$ (525.86) Calcd. C 43.38 H 2.71 N 3.14
Found C 42.96 H 2.87 N 3.34

Bromination in dichloromethane gave **1w** containing 2-[bis(4-bromophenyl)amino]benzoic acid as side product.

2-[Bis(2,4-dibromophenyl)amino]-5-bromobenzoic Acid (**1x**): A mixture of **1w** {10.0 g, ca. 19 mmol, containing small amounts of 2-[bis(4-bromophenyl)amino]benzoic acid} was treated with 9.12 g (57 mmol) of bromine in 50 ml of dichloromethane. After 24 h, unreacted bromine was removed by the addition of dilute NaOH, then the solution was acidified and extracted with dichloromethane. The organic phase was washed with water, dried with $MgSO_4$, and the solvent evaporated. The resulting light yellow crystals (12.0 g) were recrystallized three times from dichloromethane/petroleum ether to give 6.55 g (51%) of **1x**, m.p. >270°C. – IR (KBr): ν̃ = 1700 cm^{-1} (CO), 1465 (CN), 1305, 1240, 1200 (C–O), 820. – MS (70 eV): *m/z* (%) = 689, 687, 685, 683, 681, 679 (9, 48, 99, 100, 50, 10) [M^+], 563, 561, 559, 557, 555 (3, 12, 20, 13, 3), 527, 525, 523, 521 (6, 17, 17, 5), 483, 481, 479, 477 (4, 12, 11, 3), 446, 444, 442 (1, 2, 1).

$C_{19}H_{10}Br_5NO_2$ (638.88) Calcd. C 33.37 H 1.47 N 2.05
Found C 33.32 H 1.40 N 1.98

Methyl 2-[Bis(4-bromophenyl)amino]-5-bromobenzoate (**1y**): 150 mg (0.285 mmol) of **1w**, dissolved in 10 ml of methanol, was treated with diazomethane according to a literature procedure[53] (TLC control). After partial removal of the methanol, crystals formed in the refrigerator. The crystals were collected and washed with petroleum ether to give 150 mg (97%) of **1y**, m.p. 147°C. – IR (KBr): ν̃ = 1710 cm^{-1} (CO), 1575, 1485 (arom. CH, C–N), 1310, 1290, 1280 (C–O), 825. – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 1.8 Hz, 1H), 7.55 (dd, *J* = 9 Hz and 1.8 Hz, 1H), 7.03 (d, *J* = 9 Hz, 1H), 7.38–7.28 and 6.89–6.79 (AA'BB', 8H, C_6H_4), 3.43 (s, 3H, CH_3). – ^{13}C NMR (22.5 MHz, $CDCl_3$): δ = 165.82 (CO), 146.11 (arom. C), 144.81 (arom. C), 136.04 (arom. CH), 134.42 (arom. CH), 132.35 (2 arom. CH), 130.77 (arom. CH), 130.41 (arom. C), 124.36 (2 arom. CH), 118.05 (arom. CBr), 115.59 (arom. CBr), 52.27 (CH_3). – MS (70 eV): *m/z* (%) = 543, 541, 539, 537 (37, 100, 100, 37) [M^+], 462, 460, 458 (2, 4, 2), 431, 429, 427 (4, 6, 4), 403, 401, 399 (11, 22, 11), 241 (11), 121 (11). – UV ($CHCl_3$): λ_{max} (lg ε) = 360 nm (3.63), 308 (4.49).

$C_{20}H_{14}Br_3NO_2$ (540.088) Calcd. C 44.48 H 2.61 N 2.59
Found C 44.70 H 2.69 N 2.49

4-Nitrobenzyl 2-[Diphenylamino]benzoate: 5.80 g (20 mmol) of 2-(diphenylamino)benzoic acid and 6.45 g (30 mmol) of 4-nitro-benzyl bromide were dissolved in 350 ml of $CHCl_3$, and the solution was heated to reflux for 5 d and then filtered while hot. After cooling, the organic phase was washed with dilute NaOH, water, and NaCl solution, dried with $MgSO_4$, and the solvent was evaporated. The residue was recrystallized from ethanol/petroleum ether to give 6.70 g (79%) of produkt, m.p. 114–115°C (green crystals). – IR (KBr): ν̃ = 1720 cm^{-1} (CO), 1595, 1585, 1490 (arom. CH), 1480 (C–N), 1520, 1350 (NO_2), 1290, 1125 (C–O), 855, 840, 755, 695. – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 8.13–6.92 (m, 18H), 4.96 (s, 2H, CH_2Ph). – MS (70 eV): *m/z* (%) = 424 (100) [M^+], 289 (8), 272 (20), 245 (8), 244, 243 (12), 167 (7), 166 (6). – UV ($CHCl_3$): λ_{max} (lg ε) = 357 nm (3.5), 295 (4.32), 262 (4.15).

$C_{26}H_{20}N_2O_4$ (424.53) Calcd. C 73.57 H 4.75 N 6.6
Found C 73.83 H 4.62 N 6.75

4-Nitrobenzyl 2-[Bis(4-bromophenyl)amino]-5-bromobenzoate (**1z**): 3.00 g (7.0 mmol) of 4-nitrobenzyl 2-(diphenylamino)benzoate, dissolved in 20 ml of $CHCl_3$, was treated with 3.36 g (21 mmol) of bromine and stirred for ca. 12 h. The reaction mixture was washed with water, dried with $MgSO_4$, the solvent partially removed in vacuo, and a layer of petroleum ether was put on top of the remaining organic phase. The crystals thus formed were washed with petroleum ether to give 3.10 g (66%) of **1z**, m.p. 88–92°C. – IR (KBr): ν̃ = 1725 cm^{-1} (CO), 1610, 1580, 1490 (arom. CH), 1530 (C–NO_2), 1470 (C–N), 1350, 1315, 1285, 830, 865, 740. – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 1.8 Hz, 1H), 7.60 (dd, *J* = 9 Hz and 1.8 Hz, 1H), 7.05 (d, *J* = 9 Hz, 1H), 8.23–8.13 and 7.33–7.23 (AA'BB', 4H, C_6H_4), 7.33–7.22 and 6.85–6.76 (AA'BB', 8H, C_6H_4), 4.94 (s, 2H, CH_2Ph). – MS (70 eV): *m/z* (%) = 664, 662, 660, 658 (32, 100, 100, 31) [M^+], 584, 582, 580 (7, 15, 7), 529, 527, 525 (4, 6, 4), 431, 429, 427 (4, 9, 5), 403, 401, 399 (11, 23, 11), 241 (24). – UV ($CHCl_3$): λ_{max} (lg ε) = 357 nm (3.5), 295 (4.32), 262 (4.15).

$C_{26}H_{17}Br_3N_2O_4$ (661.252) Calcd. C 47.23 H 2.59 N 4.24
Found C 47.62 H 2.38 N 4.15

Tris(4-perfluoroalkylphenyl)amines

Tris(4-trifluoromethylphenyl)amine (**1za**): The starting materials 4-(trifluoromethyl)aniline, (4-trifluoromethyl)acetanilide, and 1-bromo-4-trifluoromethylbezene were prepared by literature procedures[54,55,56]. 6.50 g (29.0 mmol) of 1-bromo-4-trifluoromethylbenzene, 2.93 g (14.4 mmol) of 4-trifluoromethylacetanilid, 1.99 g of K_2CO_3, 3 ml of nitrobenzene, and 0.87 g of a mixture of equal amounts of CuI and Cu powder were heated at reflux for 17 h. After workup according to the literature[58,59] and distillation, the crude product was chromatographed on silica gel by using dichloromethane/petroleum ether (1:10) as eluent. Besides 920 mg (22%) of bis(4-trifluoromethylphenyl)amine, 232 mg (3.6%) of **1za** was isolated, m.p. 171–174°C. – IR (KBr): ν̃ = 2945 cm^{-1} (CH), 1615, 1520 (arom. CH), 1140–1120, 1075 (CF_3), 845. – ^{1}H NMR (90 MHz, $CDCl_3$): δ = 7.6–7.5 and 7.21–7.11 (AA'BB', 12H, C_6H_4). – MS (70 eV): *m/z* (%) = 449 (100) [M^+], 448 (8), 447 (3), 430 (19), 428 (3), 380 (7), 379 (11), 311 (5). – UV ($CHCl_3$): λ_{max} (lg ε) = 308 nm (3.45), 285 (3.05), 242 (2.82).

$C_{21}H_{12}F_9N$ (M^+) Calcd. 449.0826 Found 449.0822 (MS)

Tris(4-pentafluoroethylphenyl)amine (**1zb**): A mixture of 0.50 g (1.03 mmol) of **1c**, 1.00 g of freshly prepared Cu powder[60], and 4 ml of dry DMF in a bomb tube was cooled to −78°C. After the addition of 4 ml of pentafluoroethyl iodide, the bomb tube was carefully closed and heated to 80°C for 12 h followed by 9 h at 140°C. After opening the reaction vessel at −78°C and warming to room temp., the unreacted pentafluoroethyl iodide was evaporated followed by the addition of water and $CHCl_3$. The solution was filtered, the organic phase washed with large amounts of water, dried with $MgSO_4$, and the solvent evaporated. The crude product was recrystallized three times from CH_3CN/MeOH to yield 135 mg (22%) of **1zb** still containing traces of other triarylamines. − IR (KBr): $\tilde{\nu}$ = 1615 cm^{-1}, 1525 (arom. CH), 1290, 1220, 1105 (CF), 845, 770. − ^1H NMR (90 MHz, $CDCl_3$): δ = 7.59−7.49 and 7.25−7.15 (AA'BB', 12H, C_6H_4). − MS (70 eV): *m/z* (%) = 599 (84) [M^+], 580 (9), 533 (100).

$C_{24}H_{12}F_{15}N$ (M^+) Calcd. 599.0730 Found 599.0772 (MS)

Synthesis of Brominated Acridones

2,7-Dibromo-10-(4-bromophenyl)acridone (**2a**): According to a literature procedure[61], 350 mg (0.66 mmol) of **1w** in 2 ml of concd. H_2SO_4 was heated to 100°C for 1 h. After the addition of water, the solution was filtered, the residue washed with $NaHCO_3$ solution and water, dried, and recrystallized from toluene to give 320 mg (94%) of **2a**, m.p. >270°C. − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1} (arom. CH), 1635 (CO), 1595, 1480 (arom. CH, CN), 1205 (C−O), 830, 810. − ^1H NMR (90 MHz, [D$_6$]DMSO): δ = 8.57 (d, *J* = 2.7 Hz, 2H), 7.67 (dd, *J* = 8.2 and 2.7 Hz, 2H), 7.99−7.89 and 7.41−7.31 (AA'BB', 4H, C_6H_4), 6.75 (d, *J* = 8.2 Hz, 2H). − MS (70 eV): *m/z* (%) = 511, 509, 507, 505 (34, 100, 100, 34) [M^+], 430, 428, 426 (1, 2, 1), 349, 347 (2.5, 2.5), 321, 319 (2.5, 2.5), 240 (8), 120 (7). − UV ($CHCl_3$): λ_{max} (lg ε) = 408 nm (4.09), 389 (3.97), 370 (3.64), 318 (3.58), 304 (3.68), 282 (4.64), 254 (4.63).

$C_{19}H_{10}Br_3NO$ (508.045) Calcd. C 44.92 H 1.98 N 2.76
Found C 44.70 H 1.86 N 2.56

2,4,7-Tribromo-10-(2,4-dibromophenyl)acridone (**2b**): 4.98 g (7.3 mmol) of **1x** was dissolved in 10 ml of concd. H_2SO_4 and heated to 100°C for 2 h. After the addition of water, the solution was filtered and the yellow residue recrystallized from 200 ml of toluene (the product was insoluble in CH_3CN, CH_2Cl_2, and only slightly soluble in benzonitrile) to give 4.00 g (85%) of **2b**, m.p. >270°C. − IR (KBr): $\tilde{\nu}$ = 1635 cm^{-1} (CO), 1600, 1580, (arom. CH), 1470 (C−N), 1310, 1285, 1145, 840, 810, 780, 750. − ^1H NMR (90 MHz, [D$_6$]DMSO): δ = 8.55 (d, *J* = 2.6 Hz, 1H), 8.43 (d, *J* = 2.4 Hz, 1H), 8.3 (d, *J* = 2.4 Hz, 1H), 8.26 (d, *J* = 2 Hz, 1H), 7.94 (dd, *J* = 9.4 and 2 Hz, 1H), 7.87 (dd, *J* = 9.4 and 2.6 Hz, 1H), 6.77 (d, *J* = 9.4 Hz, 1H), 6.75 (d, *J* = 9.4 Hz, 1H). − MS (70 eV): *m/z* (%) = 671, 669, 667, 665, 663, 661 (10, 49, 98, 100, 51, 10) [M^+], 591, 589, 587, 585, 583 (4, 13, 23, 19, 7), 509, 507, 505, 503 (13, 39, 39, 13), 428, 426, 424 (2, 8, 3), 400, 398, 396 (1, 3, 1), 347, 345 (8, 8), 319, 317 (8, 8). − UV ($CHCl_3$): λ_{max} (lg ε) = 407 nm (4.12), 388 (3.99), 369 (3.71), 318 (3.86), 287 (4.46), 282 (4.5), 268 (4.6), 258 (4.53), 246 (4.57).

$C_{19}H_8Br_5NO$ (665.861) Calcd. C 34.28 H 1.21 N 2.10
Found C 34.68 H 1.15 N 1.94

1,3,6,8-Tetrabromo-9-(4-bromophenyl)carbazole (**3b**): A mixture of 12.7 g (45 mmol) of 1-iodo-4-bromobenzene, 14.6 g (30 mmol) of 1,3,6,8-tetrabromocarbazole[62], 6.70 g (50 mmol) of dry K_2CO_3, and some milligrams of copper powder was heated to 240°C for 6 h. The solid reaction mixture was continuously extracted with acetone for 8 h. After evaporation of the solvent, the crude product was recrystallized from dichloromethane to give 7.00 g (37%) of **3b**, contaminated with equal amounts of 1,3,6,8-tetrabromo-9-(4-iodophenyl)carbazole which could neither be removed by HPLC nor by recrystallization. − ^1H NMR (90 MHz, $CDCl_3$): δ = 7.13−7.88 (m, 1/2 × 4H, C_6H_4I), 7.26−7.70 (m, 1/2 × 4H, C_6H_4Br), 7.77 (d, *J* = 1.9 Hz, 2H), 8.15 (d, *J* = 1.9 Hz, 2H). − MS (70 eV): *m/z* (%) = 689, 687, 685, 683, 681 (17, 67, 100, 66, 16) [M^+; 4'-iodo derivative], 643, 641, 639, 637, 635, 633 (10, 49, 98, 100, 51, 11) [M^+; 4'-bromo derivative], 562, 560, 558, 556, 554 (1, 4, 6, 4, 1), 481, 479, 477, 475 (9, 27, 27, 9), 319, 317 (18, 18), 239 (39), 238 (40).

N,N,N',N'-Tetrakis(4-bromophenyl)-p-phenylenediamine (**4a**): To a solution of 3.00 g (7.3 mmol) of *N,N,N',N'*-tetraphenyl-*p*-phenylenediamine in 50 ml of $CHCl_3$ a solution of 4.66 g (29 mmol) of bromine, dissolved in $CHCl_3$ (50 ml), was slowly added. At the end of the addition, a precipitate had formed. After heating at reflux for 20 min, the hot solution was filtered. On cooling to room temp., **4a** precipitated. The crystals were collected and washed with cold $CHCl_3$ or diethyl ether. After evaporation of some $CHCl_3$ from the filtrate, a second crop of **4a** was obtained to give 3.00 g (56%) of **4a**, m.p. 280−284°C.

$C_{30}H_{20}Br_4N_2$ (728.17) Calcd. C 49.48 H 2.77 N 3.85
Found C 49.46 H 2.73 N 3.79

N,N,N',N'-Tetrakis(2,4-dibromophenyl)-p-phenylenediamine (**4b**): Under the same conditions as for **4a**, 3.00 g (7.3 mmol) of *N,N,N',N'*-tetraphenyl-*p*-phenylenediamine was treated with 9.32 g (58 mmol) of bromine to give 2.50 g (33%) of **4b**, m.p. >280°C.

$C_{30}H_{16}Br_8N_2$ (1043.80) Calcd. C 34.52 H 1.55 N 2.68
Found C 34.85 H 1.94 N 2.70

CAS Registry Numbers

1b: 1159-53-1 / **1b**$^{\bullet+}$: 34516-45-5 / **1c**: 4316-58-9 / **1i**: 20440-93-1 / **1i**$^{\bullet+}$: 34516-47-7 / **1i**$^{\bullet+}$ · $SbCl_6^-$: 135761-59-0 / **1n**: 135761-31-8 / **1n**$^{\bullet+}$: 135761-47-6 / **1n**$^{\bullet+}$ · $SbCl_6^-$: 135761-60-3 / **1o**: 135761-32-9 / **1o**$^{\bullet+}$ · $SbCl_6^-$: 135789-14-9 / **1p**: 135761-33-0 / **1q**: 135761-34-1 / **1r**: 83026-10-2 / **1r**$^{\bullet+}$: 135761-52-3 / **1s**: 135761-57-8 / **1t**: 135761-35-2 / **1t**$^{\bullet+}$: 135761-48-7 / **1u**: 135761-36-3 / **1u**$^{\bullet+}$: 135761-53-4 / **1v**: 118996-38-6 / **1w**: 135761-37-4 / **1w**$^{\bullet+}$: 135761-49-8 / **1x**: 135761-38-5 / **1y**: 135761-39-6 / **1y**$^{\bullet+}$: 135761-54-5 / **1y**$^{\bullet+}$ · $SbCl_6^-$: 135761-61-4 / **1z**: 135761-40-9 / **1z**$^{\bullet+}$: 135761-50-1 / **1z**$^{\bullet+}$ · $SbCl_6^-$: 135761-62-5 / **1za**: 135761-41-0 / **1za**$^{\bullet+}$: 135761-55-6 / **1za**$^{\bullet+}$ · $SbCl_6^-$: 135761-63-6 / **1zb**: 135761-42-1 / **1zb**$^{\bullet+}$: 135761-51-2 / **2a**: 135761-43-2 / **2b**: 135761-44-3 / **3a**: 73087-83-9 / **3a**$^{\bullet+}$: 73087-86-2 / **3a**$^{\bullet+}$ · $SbCl_6^-$: 135761-64-7 / **3b**: 135761-45-4 / **4a**: 111017-60-8 / **4b**: 135761-46-5 / triphenylamine: 603-34-9 / diphenyl(4-trifluoroacetylphenyl)amine: 135761-56-7 / bis(4-nitrophenyl)phenylamine: 1100-10-3 / 2-(diphenylamino)benzoic acid: 17626-44-7 / 4-nitrobenzyl bromide: 100-11-8 / 4-nitrobenzyl 2-(diphenylamino)benzoate: 135761-58-9 / 1-bromo-4-trifluoromethylbenzene: 402-43-7 / 4-trifluoromethylacetanilid: 349-97-3 / bis(4-trifluoromethylphenyl)amine: 7639-71-6 / pentafluoroethyl iodide: 354-64-3 / 1-iodo-4-bromobenzene: 589-87-7 / 1,3,6,8-tetrabromocarbazole: 55119-09-0 / *N,N,N',N'*-tetraphenyl-*p*-phenylenediamine: 14118-16-2

[1] Part I: W. Schmidt, E. Steckhan, *Chem. Ber.* **1980**, *113*, 577−585.
[2] E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, R. N. Adams, *J. Am. Chem. Soc.* **1966**, *88*, 3498−3503.
[3] E. Steckhan, *Angew. Chem.* **1986**, *98*, 681−699; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 683-701; *Top. Curr. Chem.* **1987**, *142*, 1−70.
[4] W. Schmidt, E. Steckhan, *Angew. Chem.* **1978**, *90*, 717; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 673−674; *ibid.* **1979**, *91*, 850−851; *ibid.* **1979**, *18*, 801−802; *ibid.* **1979**, *91*, 851−852; *ibid.* **1979**, *18*, 802−803; T. Esch, Diploma Thesis, University of Bonn, **1983**, Ph. D. Thesis, University of Bonn, **1987**; S. Mavili, Ph. D. Thesis, University of Bonn, **1991**.
[5] T. R. Hoye, M. J. Kurth, V. Lo, *Tetrahedron Lett.* **1981**, *22*, 815−818.
[6] S. Dapperheld, E. Steckhan, *Angew. Chem.* **1982**, *94*, 785; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 780−781; *Angew. Chem. Suppl.* **1982**, 1730−1731.

[7] M. Platen, E. Steckhan, *Tetrahedron Lett.* **1988**, *21*, 511–514; *Chem. Ber.* **1984**, *117*, 1679–1694; N. Schultz, S. Töteberg-Kaulen, S. Dapperheld, J. Heyer, M. Platen, and K. Schumacher, *Recent Advances in Electroorganic Synthesis*, Proc. of the 1st International Symposium on Electroorganic Synthesis, Kodansha, Tokyo, Elsevier, Amsterdam, **1987**, pp. 127–135.
[8] M. Platen, E. Steckhan, *Liebigs Ann. Chem.* **1984**, 1563–1576;
[9] S. Töteberg-Kaulen, Ph. D. Thesis, University of Bonn, **1986**; N. Schultz, S. Töteberg-Kaulen, S. Dapperheld, J. Heyer, M. Platen, K. Schumacher, *Recent Advances in Electroorganic Synthesis*, Proc. of the 1st International Symposium on Electroorganic Synthesis, Kodansha, Tokyo, Elsevier, Amsterdam, **1987**, pp. 127–135.
[10] A. Marra, J.-M. Mallet, C. Amatore, P. Sinay, *Synlett* **1990**, 572–574.
[11] J. Heyer, S. Dapperheld, E. Steckhan, *Chem. Ber.* **1988**, *121*, 1617–1623.
[12] K. H. Grosse Brinkhaus, E. Steckhan, D. Degner, *Tetrahedron* **1986**, *42*, 533–560.
[13] D. Pletcher, G. D. Zappi, *J. Electroanal. Chem.* **1989**, *270*, 401–405.
[14] K. H. Grosse Brinkhaus, E. Steckhan, W. Schmidt, *Acta Chem. Scand., Ser. B* **1983**, *37*, 499–507.
[15] K. D. Ginzel, E. Steckhan, D. Degner, *Tetrahedron* **1987**, *43*, 5797–5805.
[16] V. Calo, L. Lopez, L. Troisi, *J. Chem. Soc., Chem. Commun.* **1989**, 25–26.
[17] D. Pletcher, G. D. Zappi, *J. Electroanal. Chem.* **1989**, *265*, 203–213; B. Wierlemann, Diploma Thesis, University of Münster, **1982**.
[18] M. Schmittel, U. Baumann, *Angew. Chem.* **1990**, *102*, 571–572; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 541–542; M. Schmittel, A. Abufarag, O. Luche, M. Levis, *Angew. Chem.* **1990**, *102*, 1174–1176; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1144–1146; M. Schulz, R. Kluge, L. Sivilai, B. Kamm, *Tetrahedron* **1990**, *46*, 2371–2380.
[19] J. Gunic, I. Tabakovic, Z. Sanicanin, *Electrochim. Acta* **1990**, *35*, 225–228.
[20] J. M. Kern, D. Martina, M. P. Heitz, *Tetrahedron Lett.* **1985**, *26*, 737–740.
[21] N. L. Bauld, *Tetrahedron* **1989**, *45*, 5307–5363; J. Mattay, G. Trampe, J. Rusnik, *Chem. Ber.* **1988**, *121*, 1991–2005; K. T. Lorenz, N. L. Bauld, *J. Am. Chem. Soc.* **1987**, *109*, 1157–1160; N. L. Bauld, D. J. Bellville, B. Harirchian, K. T. Lorenz, R. A. Pabon, Jr., D. W. Reynolds, D. D. Wirth, H.-S. Chiou, B. K. Marsh, *Acc. Chem. Res.* **1987**, *20*, 371–378, and literature cited therein; A. G. Davies, R. Hay-Motherwell, *J. Chem. Soc., Perkin Trans. 2* **1988**, 2099–2103; L. Eberson, B. Olofsson, *Acta Chem. Scand.* **1991**, *45*, 316–326; L. Eberson, B. Olofsson, submitted for publication in *Acta Chem. Scand.*
[22] S. F. Nelson, *Acc. Chem. Res.* **1987**, *20*, 269–276, and literature cited therein; S. F. Nelsen, M. F. Teasley, D. L. Kapp, *J. Am. Chem. Soc.* **1986**, *106*, 5503–5509; E. L. Clennan, W. Simmons, C. W. Almgren *J. Am. Chem. Soc.* **1981**, *103*, 2098–2099.
[23] D. H. R. Barton, R. K. Haynes, G. Leclerc, P. D. Magnus, I. D. Menzies, *J. Chem. Soc., Perkin. Trans. 1* **1975**, 2055–2065, and references therein.
[24] H. Ikeda, Y. Yamashita, C. Kabuto, T. Miyashi, *Chem. Lett.* **1988**, 1333–1336; P. G. Gassman, J. W. Hershberger, *J. Org. Chem.* **1987**, *52*, 1337–1339; R. W. Hoffmann, W. Barth, *J. Chem. Soc., Chem. Commun.* **1983**, 345–346.
[25] H. Wieland, E. Wecker, *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 699–712.
[26] R. I. Walter, *J. Am. Chem. Soc.* **1955**, *77*, 5999–6002.
[27] R. G. R. Bacon, S. C. Rennison, *J. Chem. Soc. C* **1969**, 312–315; L. Eberson, B. Larsson, *Acta Chem. Scand., Ser. B* **1986**, *40*, 210–225.
[28] H. Wieland, *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 4260–4281.
[29] T. N. Baker, III, W. P. Doherty, Jr., W. S. Kelley, W. Newmeyer, J. E. Rogers, Jr., R. E. Spalding, R. I. Walter, *J. Org. Chem.* **1965**, *30*, 3714–3718; R. Reynolds, L. L. Line, R. F. Nelson, *J. Am. Chem. Socc.* **1974**, *96*, 1087–1092.
[30] F. A. Bell, A. Ledwith, D. C. Sherrigton, *J. Chem. Soc. C* **1969**, 2719–2720.
[31] W. S. Kelley, L. Monack, P. T. Rogge, R. N. Schwartz, S. P. Varimbi, R. I. Walter, *Liebigs Ann. Chem.* **1971**, *744*, 129–141.
[32] R. I. Walter, *J. Am. Chem. Soc.* **1953**, *75*, 2771–2772.
[33] G. A. Pearson, M. Rocek, R. I. Walter, *J. Phys. Chem.* **1978**, *82*, 1185–1192.
[34] E. Steckhan, *Organic Electrochemistry* (Eds.: H. Lund, M. M. Baizer), 3rd ed., Marcel Dekker, Inc., New York, **1991**, pp. 592–594.
[35] F. Ullmann, *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 2382–2384.
[36] H. Schrage, F. Vögtle, E. Steckhan, *J. Incl. Phenom.* **1988**, *6*, 157–165.
[37] P. Buck, G. Köbrich, *Tetrahedron Lett.* **1967**, 1563–1565; G. Köbrich, P. Buck, *Chem. Ber.* **1970**, *103*, 1412–1419.
[38] A. J. Bard, L. R. Faulkner, *Electrochemical Methods*, Wiley & Sons, New York, **1980**, p. 213.
[39] Ref.[38], p. 229.
[40] R. I. Walter, *J. Am. Chem. Soc.* **1966**, *88*, 1923–1937.
[41] F. A. Neugebauer, S. Bamberger, W. R. Groh, *Chem. Ber.* **1975**, *108*, 2406–2415.
[42] M. Mohammed, B. R. Sundheim, *Theor. Chim. Acta* **1968**, *10*, 222–230.
[43] G. N. Lewis, E. Lipkin, *J. Am. Chem. Soc.* **1942**, *64*, 2801–2808.
[44] D. Holtz, *Chem. Rev.* **1971**, *71*, 139–145; *Prog. Phys. Org. Chem.* **1971**, *8*, 1–74.
[45] O. Exner in *Correlation Analysis in Chemistry* (Eds.: N. B. Chapman, J. Shorter), Plenum Press, New York, **1978**, p. 439.
[46] E. Ahlberg, B. Helgee, V. D. Parker, *Acta Chem. Scand., Ser. B* **1986**, *34*, 187–193.
[47] L. Eberson, B. Larsson, *Acta Chem. Scand., Ser. B* **1986**, *40*, 210–225.
[48] K. H. Grosse Brinkhaus, Ph. D. Thesis, University of Bonn, **1984**.
[49] S. Dapperheld, Ph. D. Thesis, University of Bonn, **1984**.
[50] L. Eberson, B. Larsson, *Acta Chem. Scand., Ser. B* **1987**, *41*, 367–378.
[51] L. Eberson, B. Olofsson, *Acta Chem. Scand.*, in press.
[52] G. Wittig, U. Schöllkopf, *Chem. Ber.* **1954**, *87*, 1318–1330.
[53] S. P. Sorensen, W. H. Bruning, *J. Am. Chem. Soc.* **1973**, *95*, 2445–2451.
[54] L. F. Fieser, M. Fieser, *Reagents for Organic Synthesis*, J. Wiley & Sons, New York, **1969**, vol. 1, p. 191.
[55] R. G. Jones, *J. Am. Chem. Soc.* **1947**, *69*, 2346–2350.
[56] H. Fisher, *J. Am. Chem. Soc.* **1934**, *56*, 2469–2470.
[57] M. Markarian, *J. Am. Chem. Soc.* **1952**, *74*, 1858–1859.
[58] A. Roe, J. A. Montgommery, W. A. Yarnall, V. A. Hoyle, Jr., *J. Org. Chem.* **1956**, *21*, 28–31.
[59] A. Roe, W. F. Little, *J. Org. Chem.* **1955**, *20*, 1577–1590.
[60] T. Yamamoto, *Synth. Commun.* **1979**, *9*, 219–22.
[61] I. Goldberg, D. Nimerovsky, *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 2448–2452.
[62] J. Pielichowski, J. Kyziol, *Monatsh. Chem.* **1974**, *105*, 1306–1312.
[63] T. Esch, Ph. D. Thesis, University of Bonn, **1983**.

[213/91]