

Aminobenzenes. 19.¹ Dimeric σ -Complexes: Intermediates in the Oxidative Dimerization of Aromatics

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Dimeric σ -complexes **2**, postulated intermediates in the oxidative dimerization of aromatics, were obtained by oxidation of tripyrrolidin-1-ylbenzenes **1a-f** with silver nitrate. Treatment of **2** with strong base gave biphenyls **4**. In solution, especially under the influence of light, compounds **2** dissociate to radical cations **1^{•+}**, which react irreversibly with solvent under H abstraction to give σ -complexes **3**. Crystal structures were determined by X-ray diffraction methods for compounds **2a** and **2c**. Reactions of triaminobenzenes **8** and **9** with bromine and halocyanogens gave mixtures of substitution (**10/11**) and dimerization products (**12/13**). This product formation can be plausibly explained in terms of known steric and electronic factors of both reaction partners.

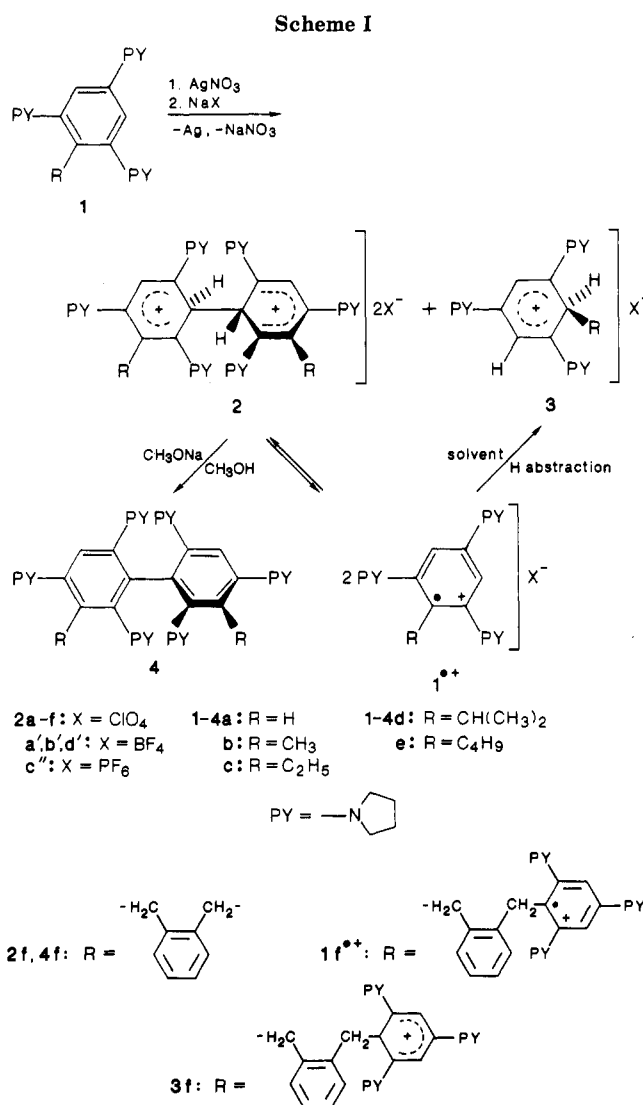
Introduction

Several alternative mechanisms have been discussed² for oxidative dimerization of aromatics. In all cases, the first reaction step is assumed to be oxidation of the aromatic to radical cations. The postulation of dimeric σ -complexes as intermediates is also common to all of the proposed mechanisms. Their subsequent deprotonation gives rise to diaryls as the first isolable oxidation products. Whether the dimeric σ -complexes arise from dimerization of the radical cations, by electrophilic reaction of dications formed by further oxidation of radical cations with the starting aromatics, or by oxidation of the 1:1 adducts from radical cations and the starting aromatics is an open question of considerable importance to the understanding of the mechanism of oxidative dimerization. In a previous study,³ we reported on the oxidation and halogenation of symmetrical triaminobenzenes in which dimeric σ -complexes obtained by oxidation and halogenation were isolated for the first time. In the belief that further insight into the mechanism of dimerization of aromatic compounds could be gained, we have pursued a detailed study of the formation and especially the structural properties of these interesting reaction intermediates.

In view of the very intensive recent interest⁴ in the structural features of radical cation salts, which are potential organic conductors, accurate information on the structure of dimeric σ -complexes should be valuable.

Oxidation of Tripyrrolidin-1-ylbenzenes

The reaction of 1,3,5-tripyrrolidin-1-ylbenzene (**1a**) or of the 2-alkyl-1,3,5-tripyrrolidin-1-ylbenzenes **1b-f** with silver nitrate in acetonitrile (Scheme I) gives rise to immediate formation of a deep red color accompanied by simultaneous precipitation of elemental silver. Aqueous



(1) For part 18, see: Schöllkopf, K.; Stezowski, J. J.; Effenberger, F. *Organometallics* **1985**, *4*, 922-929.

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(4) (a) Fritz, H. P.; Gebauer, H.; Friedrich, P.; Schubert, U. *Angew. Chem.* **1978**, *90*, 305-306; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 275. (b) Kröhnke, C.; Enkelmann, V.; Wegner, G. *Angew. Chem.* **1980**, *92*, 941-942; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 912.

workup of the reaction mixture with addition of sodium perchlorate, sodium tetrafluoroborate, or sodium hexafluorophosphate results in precipitation of 2,2',4,4',6,6'-hexapyrrolidin-1-yl-1,1'-bicyclohexadienylium complexes **2** as stable salts (Table I).

In solution, the alkyl-substituted dimeric σ -complexes **2** dissociate easily to radical cations **1^{•+}**, which, in addition to the reverse dimerization reaction, via hydrogen abstraction from the solvent, can form the monomeric σ -

Table I. Oxidation of 1,3,5-Tripyrrolidin-1-ylbenzenes 1 with Silver Nitrate to 2,2',4,4',6,6'-Hexapyrrolidin-1-yl-1,1'-bicyclohexadienylium Complexes 2

1	3,3'-R	product bicyclohexadienylium	yield, %
1a	H	2, diperchlorate	86
		2a', bis(tetrafluoroborate)	88
1b	CH ₃	2b, diperchlorate	21 ^a
		2b', bis(tetrafluoroborate)	b
1c	C ₂ H ₅	2c, diperchlorate	92
		2c', bis(hexafluorophosphate)	73
1d	CH(CH ₃) ₂	2d, diperchlorate	37 ^a
		2d', bis(tetrafluoroborate)	b
1e	C ₄ H ₉	2e, diperchlorate	27 ^a
1f	CH ₂ C ₆ H ₄ CH ₂ (ortho)	2f, diperchlorate	57

^a After separation from the resulting mixture of 2/3. ^b Not determined.

complexes 3. In order to minimize these secondary reactions of compounds 2, it proved to be advantageous to carry out the reactions rapidly in the dark under nitrogen at 0 °C and to work up the reaction mixtures quickly. In this way we succeeded in preparing the 2,2',4,4',6,6'-hexapyrrolidin-1-yl-1,1'-bicyclohexadienylium diperchlorates 2a-f, the bis(tetrafluoroborates) 2a',b',d', and the bis(hexafluorophosphate) 2c' in analytically pure form (Table I).

In the case of reactions of 2-methyl- (1b), 2-isopropyl- (1d), and 2-butyl-1,3,5-tripyrrolidin-1-ylbenzene (1e), the resulting reaction products 2b,d,e were shown by ¹H NMR spectroscopic methods to be contaminated with monomeric σ -complexes 3b,d,e, which could be removed by washing with aqueous methanol, but with substantial loss of yield in 2 (Table I).

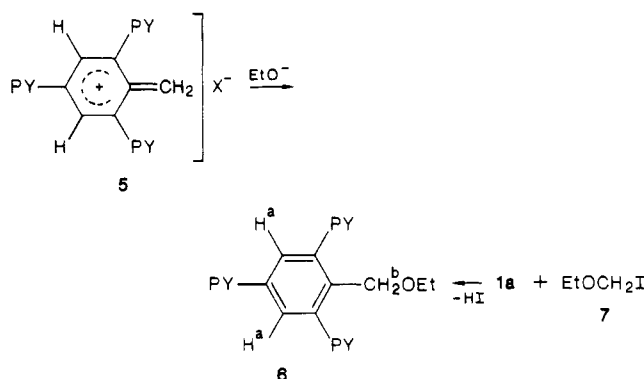
The ¹H NMR data show that the "olefinic" protons of the dimeric and monomeric σ -complexes 2 and 3 appear at practically the same field. In contrast, the protons bonded to the sp³-hybridized carbon atoms of the dimers 2 are shifted to lower fields, whereas those of the monomeric complexes 3 lie under the H_{PY α} signals (PY = pyrrolidin-1-yl) and could only be determined by integration. In a 300-MHz spectrum of the 3-ethyl-substituted monomer 3c, we obtained separation of the 1-H and H_{PY α} signals while the CH₂CH₃-proton signals from the ethyl group remained under the H_{PY β} signals (Table II).

One piece of evidence for the structure of the dimeric σ -complexes 2 presented here (coupled via C1 and C1' and substitution with R at C3 and C3') was obtained from quantitative deprotonation to the biphenyls 4 with excess methanolate and their characterization by ¹H NMR spectroscopy (Table II). In the product mixture from oxidation of 2-methyl-1,3,5-tripyrrolidin-1-ylbenzene (1b), two further signals of equal but lower intensity appear at δ 5.03 and 6.37 in addition to the signals from σ -complexes 2b and 3b. We assume that they arise from a 2-methylene-1,3,5-tripyrrolidin-1-ylcyclohexadienylium complex 5 (Scheme II). The signal at δ 5.03 can be assigned to the two olefinic 3- and 5-protons and that at δ 6.37 to the two methylene protons. After addition of alcoholate, the ¹H NMR spectrum shows the signals of the respective 1-alkoxymethyl compound 6, which we have also prepared by reaction of 1a with the iodo ether 7 (see Experimental Section).

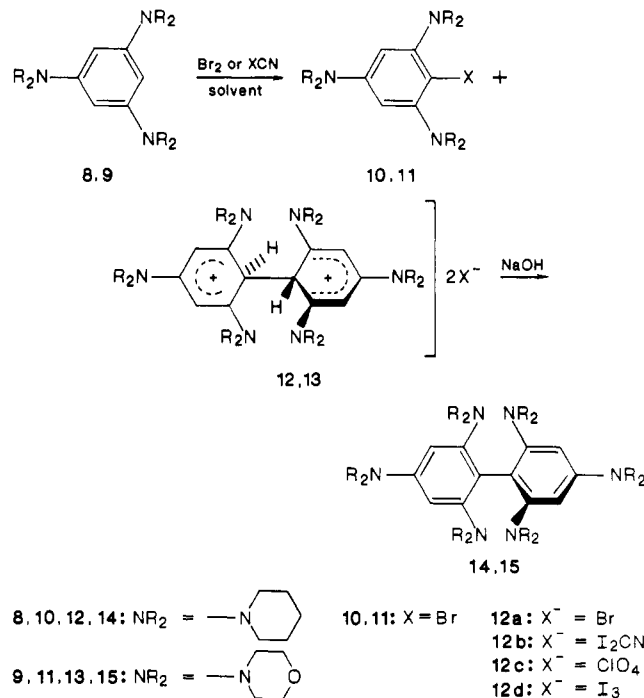
Reaction of Symmetrical Triaminobenzenes with Bromine and Halocyanogens

Reaction of 4-substituted *N,N*-dialkylanilines with bromine gives, depending on conditions, in addition to core bromination, dealkylation products and benzidines in

Scheme II



Scheme III



various quantities.⁵ The unexpected products can be explained as the result of an oxidation reaction in competition with the electrophilic substitution reaction.⁵

The reaction of *N*-peralkylated triaminobenzenes with bromine and halocyanogens was studied with two goals in mind. One was to obtain halogenated triaminobenzenes; the other was to determine the interdependence of the competing electrophilic substitution and oxidation reactions on the amino substituents, the halogenating agent, and the reaction conditions. Reaction of 1,3,5-tripiperidin-1-ylbenzene (8) with bromine or bromocyanogen gave mixtures of core bromination products 10 and dimeric σ -complexes 12a, whereas reaction with iodocyanogen gave only the oxidation product 12b (Scheme III, Table III). In contrast, the reaction of bromine or bromocyanogen with 1,3,5-trimorpholin-1-ylbenzene (9) gave only bromo compound 11, and of iodocyanogen the oxidation product 13 (Table III).

Different anions result for σ -complexes 12 and 13 depending on the halogenation agents used. As an example, we converted 12a to the stable and easy to handle perchlorate 12c by treatment with aqueous perchlorate solu-

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Table II. ¹H NMR Chemical Shifts of Dimeric 2 and Monomeric σ -Complexes 3 and of Biphenyls 4^a

A. Dimeric σ -Complexes 2 (in CD ₃ CN)					
2	5-, 5'-H (s)	1-, 1'-H (s)	6 (4 H _{PY} ^a) (m)	6 (4 H _{PY} ^b) (m)	3,3'-position
2a	4.87 ^b	4.25	3.6-3.0	2.0	2 H ^b
2b	5.03	4.06	3.8-3.0	2.0 ^c	2 CH ₃ ^c
2c	5.10	4.0	3.8-3.0	2.0	2.43 (q, 4 H, 2 CH ₂ CH ₃) 0.73 (t, 6 H, 2 CH ₂ CH ₃)
2c'' ^d	5.09 5.10	3.97 4.04	3.84-3.17	2.17-1.82	2.43 (q, 4 H, 2 CH ₂ CH ₃) 2.46 0.75 0.735 (t, 6 H, 2 CH ₂ CH ₃)
2d	5.10	3.94	3.6-3.0	1.7	3.0 (h, 2 H, 2 CH(CH ₃) ₂) 1.48 (d, 6 H, 2 CH(CH ₃)CH ₃) 1.80 (d, 6 H, 2 CH(CH ₃)CH ₃)
2e	5.06	3.98	3.7-3.0	2.0	2.4 (m, 12 H, 2 (CH ₂) ₃ CH ₃) 1.20 (m, 6 H, 2 (CH ₂) ₃ CH ₃)
2f	4.60	5.06 (d)	4.0-2.8	2.0 ^e	CH ₂ C ₆ H ₄ CH ₂ ^e 7.22 (m, 4 H, CH ₂ C ₆ H ₄ CH ₂)
B. Monomeric σ -Complexes 3 (in CDCl ₃) ^f					
3	3-, 5-H (s, 2 H)	1-H	3 (4 H _{PY} ^a) (m, 12 H)	3 (4 H _{PY} ^b) (m, 12 H)	1-position
3a	4.88	3.57 (m) ^g		2.05	H ^g
3b	4.71	3.51 (m)		2.02	1.43 (d, 3 H, CH ₃)
3c	4.95	3.88-3.61 (m)		2.06 ^h	CH ₂ CH ₃ ^h 0.79 (t, 3 H, CH ₂ CH ₃)
3c ^d	4.91	3.81 (t)	3.81-3.60 (m)	2.05- 1.88 ^h	CH ₂ CH ₃ ^h 0.75 (t, 3 H, CH ₂ CH ₃)
3d	4.90	3.57 (m)		2.06 ⁱ	CH(CH ₃) ₂ ⁱ 1.05 (d, 6 H, CH(CH ₃) ₂)
3e	4.85	3.57 (m)		2.03 ^j	CH ₂ (CH ₂) ₂ CH ₃ ^j 0.70-1.20 (m, 7 H, CH ₂ (CH ₂) ₂ CH ₃)
C. Biphenyls 4 (in CDCl ₃)					
4	3-, 3'-H (s, 2 H)	6 (4 H _{PY} ^a) (m, 24 H)	6 (4 H _{PY} ^b) (m, 24 H)	3,3'-position	
4a	5.66 ^k	3.33-2.90	1.96-1.60	2 H ^k	
4b	6.20	3.60-2.80	2.15-1.60	2.0 (s, 6 H, 2 CH ₃)	
4c	6.23	3.24-2.70	2.05-1.40	2.56 (q, 4 H, 2 CH ₂ CH ₃) 1.0 (t, 6 H, 2 CH ₂ CH ₃)	
4d	6.42	3.00 ^l	1.90-1.20	2 CH(CH ₃) ₂ ^l 1.3 (d, 12 H, 2 CH(CH ₃) ₂)	

^a60 MHz, δ , ppm. ^bSinglet, 4 H, 3-, 3'-, 5-, 5'-H. ^cMultiplet, 30 H, 24 H_{PY}^b and 6 H, 2 CH₃. ^d300-MHz spectrum. ^eMultiplet, 28 H, 24 H_{PY}^b and 4 H, CH₂C₆H₄CH₂. ^fFor preparation, see ref 9a. ^gMultiplet, 13 H, 12 H_{PY}^a and 1 H, 1-H. ^hMultiplet, 14 H, 12 H_{PY}^b and 2 H, CH₂CH₃. ⁱMultiplet, 13 H, 12 H_{PY}^b and 1 H, CH(CH₃)₂. ^jMultiplet, 14 H, 12 H_{PY}^b and 2 H, CH₂(CH₂)₂CH₃. ^kSinglet, 4 H, 3-, 3'-, 5-, 5'-H. ^lMultiplet, 26 H, 24 H_{PY}^a and 2 H, 2 CH(CH₃)₂.

Table III. Reactions of 1,3,5-Tripiperidin-1-ylbenzene (8) and 1,3,5-Trimorpholin-1-ylbenzene (9) with Bromine and Halocyanogens

educts	solvent	products	yield, %
8 + Br ₂ (1:1)	AcOH	10, 1-bromo-2,4,6-tripiperidin-1-ylbenzene	19 ^a
		+10-HBr	15 ^a
		+12a, 2,2',4,4',6,6'-hexapiperidin-1-yl-1,1'-bicyclohexadienylium dibromide	22 ^a
8 + Br ₂ (1:1) + HCl(g)	AcOH	10	66 ^a
		+12a	3 ^a
8 + BrCN (1:1)	Et ₂ O/CHCl ₃	10	74 ^a
		+12a	36 ^a
8 + ICN (1:1)	Et ₂ O/CHCl ₃	12b, 2,2',4,4',6,6'-hexapiperidine-1-yl-1,1'-bicyclohexadienylium bis(diiodocyanide)	42 ^{b,c}
8 + ICN (1:2)	Et ₂ O	12b	56 ^a
9 + Br ₂ (1:1)	AcOH	11, 1-bromo-2,4,6-trimorpholin-1-ylbenzene	45 ^b
9 + BrCN (1:1)	Et ₂ O/CHCl ₃	11	98 ^a
			70 ^b
9 + ICN (1:2)	Et ₂ O/CHCl ₃	13d, 2,2',4,4'-6,6'-hexamorpholin-1-yl-1,1'-bicyclohexadienylium complex	c,d

^aYield of the precipitated crude product. ^bPure product. ^cAdditional educt 8 or 9 was reisolated. ^dAnion for 13; see Experimental Section.

tions. By treatment with base, the σ -complexes 12 and 13 gave 2,2',4,4',6,6'-hexapiperidin-1-yl-1,1'-biphenyl (14) and 2,2',4,4',6,6'-hexamorpholin-1-yl-1,1'-biphenyl (15) in good yields.

The different product formation in the reaction of 8 and 9 with bromine and halocyanogens supports drawing conclusions about the influence of substrate, halogenating reagents, and reaction conditions on the competition of electrophilic substitution with oxidation in the reaction

of electron-rich aromatics with electrophiles.

In earlier investigations⁶ of the donor properties of dialkylamino groups, we found a similar mesomeric interaction with the aromatic ring for the morpholino residue in comparison with the piperidino group. The oxidation potential of 9 ($E_{1/2} = 0.35$ V) is significantly higher than

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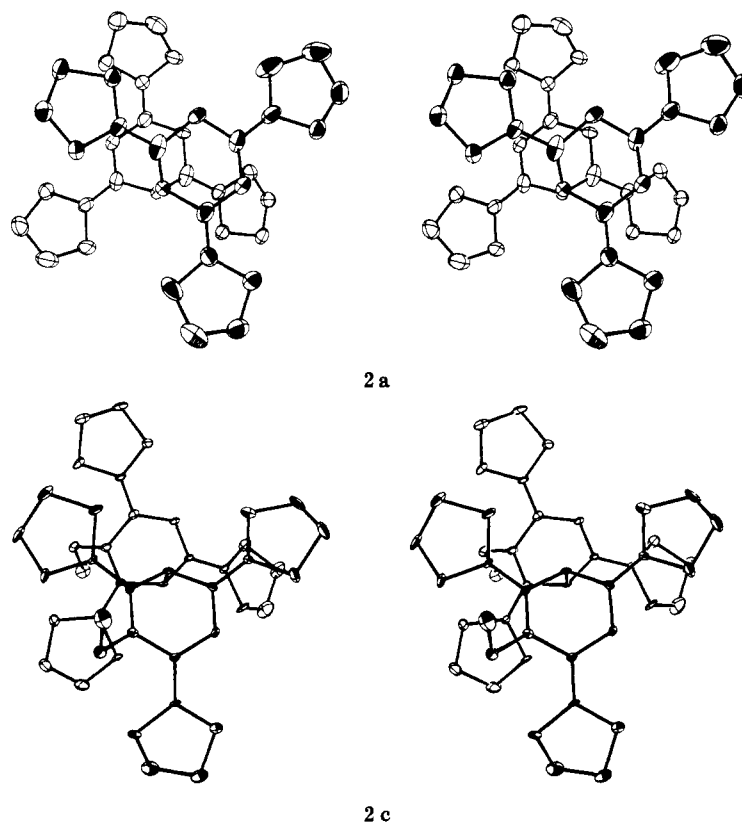


Figure 1. Stereoscopic projections illustrating the conformations of the divalent cations **2a** and **2c** (upper and lower stereoscopic pairs, respectively). To assist the viewer, the upper monomer (in the projection) is depicted with shaded ellipsoids while only the ellipsoid boundaries are drawn for the lower monomer.

that of **8** ($E_{1/2} = 0.18$ V).⁶ With the assumption that the piperidino and morpholino groups, which are both saturated six-membered ring structures and have therefore similar steric requirements, the observed product formation (Table III) is understandable as follows: Electrophilic substitution in **9**, in comparison to that in **8**, is favored, because oxidation of **9** in comparison to that of **8** is more difficult whereas σ^+ values of the piperidinyl and morpholinyl substituents are comparable. Only with ICN, which can no longer give substitution for steric reasons, **9** is oxidized to **13**. The modest fraction of oxidation products **12** resulting from reaction of **8** with bromine with simultaneous introduction of HCl is clearly the result of the increased oxidation potential of **8** by salt formation. The electrophilic substitution is apparently favored by the increasing electrophilic potential of bromine in the presence of HCl.

Oxidative dealkylation, which we found in the bromination of 4-bromo-*N,N*-dialkylanilines,⁵ was not observed in any case in the bromination of triaminobenzenes. This is in agreement with literature results,⁷ according to which the deprotonation rate in the side chain of aromatic radical cations decreases with increasing stability of the latter. Since the stability of the radical cations correlates⁷ with the ionization potential of aromatics, the lower ionization potentials of 1,3,5-tris(dialkylamino)benzenes compared with those of the *N,N*-dialkylanilines,⁸ the slower depro-

tonation rate, and the lower tendency toward dealkylation of the radical cations of the triaminobenzenes can be explained.

Structure and Properties of Dimeric σ -Complexes

We reported in detail on σ -complexes **3** (Wheland intermediates),^{9a} their crystal structure, and their structurally caused spectral properties and stabilities.^{9b} In the following discussion of the structure of dimeric σ -complexes **2a** and **2c**, we draw upon our earlier results for **3a** and **3b**; ¹H NMR chemical shifts of **3a-e** are given in Table II.

The dimeric σ -complexes are composed of two subunits coupled through a σ -bond, C1-C1'. Conformationally **2a** and **2c** (Figure 1) differ from **3a** and **3b** in that the σ -complex units of the dimers are in boat conformations, compared with either planar or bent forms for the monomers.⁹ While the structures of crystals of both compounds are disordered, the nature of the disorder and its significance for the analysis of the results differ. The disorder in the crystal of **2a**, in which the cations take on two orientations with a large number of nearly common atom sites, gave rise to a coordinate set that is not suitable for critical analysis of bonding geometry of the cation. In contrast, the disorder in the crystal for **2c** is orientational disorder in the anions and has not seriously affected the bonding geometry of the dimeric σ -complexes. The presence of two molecules per asymmetric unit in the crystal for **2c** provides two independent observations for unique bonding parameters and four for the components of the dimers (Table IV).¹⁸

(7) (a) Sehested, K.; Holcman, J. *J. Phys. Chem.* **1978**, *82*, 651-653. (b) Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7472-7482. (c) Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Phys. Chem.* **1986**, *90*, 3747-3756.

(8) (a) Koptuyug, V. A.; Rogozhnikova, O. Yu.; Detsina, A. N. *Zh. Org. Khim.* **1982**, *18*, 2017; *Chem. Abstr.* **1983**, *98*, 34160r. (b) Lias, S. G.; Jackson, J.-A. A.; Argentar, H.; Liebman, J. F. *J. Org. Chem.* **1985**, *50*, 333.

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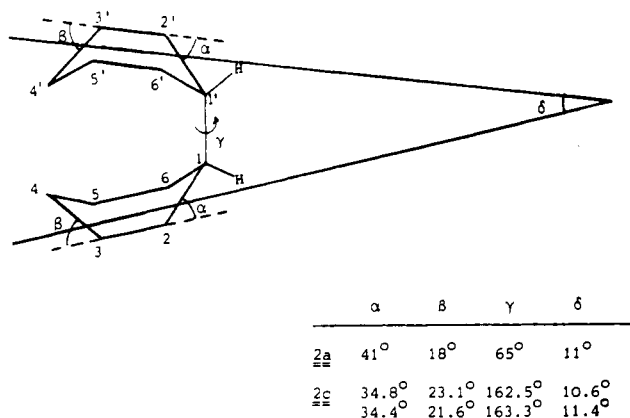


Figure 2. Characterization of the conformation of the dimers **2a** and **2c**. The values for α and β are averages for the "monomers".

The bond distances for the σ -bond joining the rings, C1-C1', are very long (average value for **2c** is 1.600 (5) Å). The H atom on C1 is equatorial, and the carbon atoms of the σ -complex units are axial (average torsion angle C1'-C1-C2-C3 = 86.7 (4)°). The mean planes fits to the respective C2, C3, C5, and C6 atoms of the cyclohexadienyl moieties within the dimer deviate significantly from being parallel (11° in **2a** and 11.4° and 10.6° in **2c**). The relative orientations of the cyclohexadienyl rings in **2a** and **2c** also differ (torsion angle C2-C1-C1'-C6' = 65° in **2a**, 162.5° and 163.3° in **2c**) (Figure 2).

These differences reflect the substitution in compound **2c** with the ethyl group at C3. There is significant asymmetry in the bonding geometry of **2c** that arises from steric interaction between substituents at positions 2, 3, and 4. Particularly noteworthy are differences in bond distances [C1-C2 > C1-C6 (0.015 Å), C2-C3 < C5-C6 (0.018 Å), C3-C4 > C4-C5 (0.041 Å), and C2-N2 > C2-N6 = C4-N4 (0.032 Å)] and in bond angles [C1-C2-C3 > C1-C6-C5 (3.3°), C1-C2-N2 < C1-C6-N6 (5.4°), C3-C2-N2 > C5-C6-N6 (2.2°), C2-C3-C4 < C4-C5-C6 (2.3°), C2-N2-C21 \approx C2-N2-C24 (0.9°), C4-N4-C41 > C4-N4-C44 (4.8°)]. Among atoms C2, C3, C4, and C6, the sums of bond angles

indicate that atom C3 deviates the most from planarity (the respective sums are 359.8°, 357.3°, 359.7°, and 359.7°); for N2, N4, and N6, the values are 359.7°, 358.6°, and 359.3°.

The bonding geometry of **2c** is consistent with the presence of hyperconjugation.⁹ The presence of extensive hyperconjugation is accompanied by lengthening of the σ -bond linking the moieties involved. The special arrangement in **2c** places the π -systems of moieties C2-C3-C5-C6 and C2'-C3'-C5'-C6' nearly parallel to the C1-C1' σ -bond. This geometry is favorable for extended interaction involving all three moieties.

The conformation of **2a** is also suitable for extensive hyperconjugation. In addition, the observed partial intramolecular overlap of the cyclopentadienyl moieties may indicate that there is also some through-space interaction between their π -systems. Unfortunately, the inaccuracies in the atomic coordinates, resulting from the disorder in the crystal, do not support closer analysis of the bonding geometry.

Through-space as well as through-bond interactions give rise to changes (band splitting and/or shifts¹⁰⁻¹³) in the long-wavelength regions of absorption spectra. UV/vis absorption spectra comparing **2a** with **3a** and **2c** with **3c** in Figure 3 display significant differences. The monomeric complexes **3a** and **3c** give simple three-band spectra. The spectra for the dimers **2a** and **2c** are more complex. The longest wavelength absorbance is split (compare the spectra of **2c** and **3c** for a particularly clear example). An additional weak shoulder occurs in the spectrum for **2a**. The solid-state (KBr pellet) spectra are qualitatively in good agreement with the solution spectra.

These crystal-structure determinations support some conclusions concerning the mechanism of the oxidative dimerization giving rise to the complexes. They provide evidence of the probable arrangements of the aromatics in the intermediate state by the formation of **2a** and **2c**. Assuming a planar structure for **1a** and [1a⁺⁺], the arrangements presented in Figure 4, with 6-fold, 2-fold, and single coordination of the two rings to each other for bond formation, are conceivable.^{14a}

Of the postulated conformations for the dimerization of aromatics^{14,15} (Figure 4), 6-C(1) would have very severe, 1-C(1) and 2-C(3) modest, and 2-C(1) the least steric interactions. Consequently, 2-C(1) is the most probable intermediate for the formation of **2a** from [1a⁺⁺], either by association of two radical cations or by reaction of a radical cation with a starting aromatic and subsequent oxidation. The observed conformation of **2a** is indeed very similar to the geometry suggested with 2-C(1), one which contains a charge transfer (CT) interaction of two π -systems.¹⁵ In the dimerization of **1c**, as molecular models show, there is an additional steric interaction between the substituents R (ethyl) and one of the pyrrolidinyl groups of the second aromatic. In this case because of the reduced steric interaction, the intermediates 1-C(1') or 1-C(2') are energetically more favorable than 2-C(1') or 2-C(2'). The conformation found for **2c** resembles the structures 1-C(1') and 1-C(2'), expected for steric reasons. In solution, two conformations were demonstrated by ¹³C and ¹H NMR spectroscopy; assignment of the spectra to 1-C(1') and 1-C(2') appears plausible.

In summary, the first isolation of dimeric σ -complexes, **2**, and the determination of their structure in the crystalline state made it possible to make more detailed statements about the dimerization of aromatics.

Experimental Section

Melting points were determined on a Büchi SMP 20 apparatus

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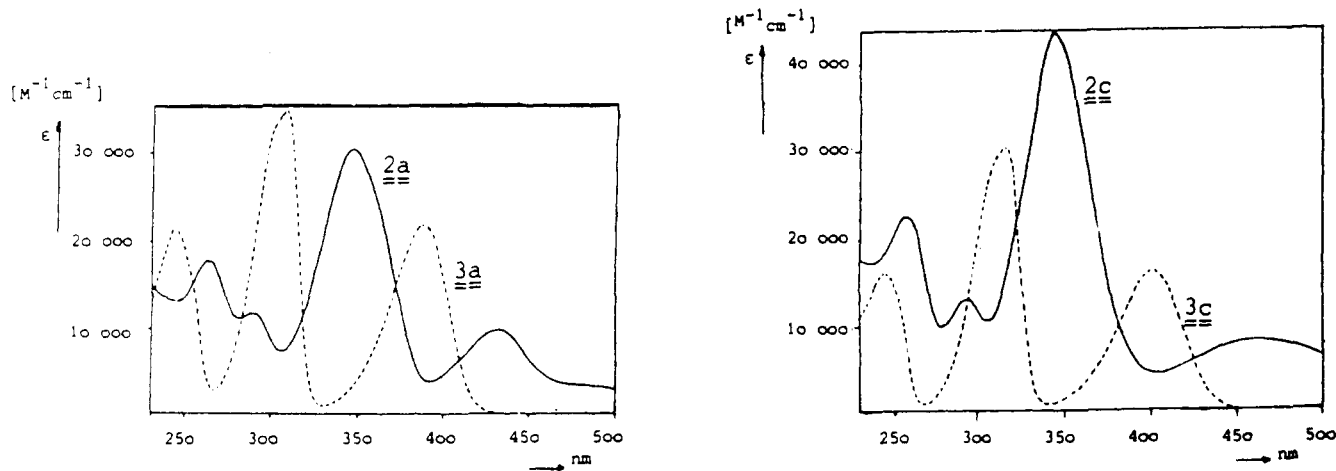


Figure 3. UV/vis absorption spectra of **2a**, **3a**, **2c**, and **3c** in acetonitrile.

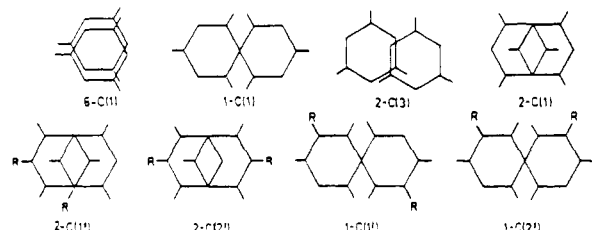


Figure 4. Postulated conformations of aromatic dimers.

with a silicon bath and are uncorrected. ^1H NMR spectra were obtained on a Varian A 60 or T 60 instrument and a Bruker WP 80 or HX 90 instrument. Chemical shifts are reported in parts per million relative to Me_4Si as an internal standard. The crystallographic data for **2a** are as follows: space group $P2_1/n$ with $a = 8.233$ (2) Å, $b = 19.887$ (6) Å, $c = 14.438$ (3) Å, $\beta = 100.82$ (2)°, and $Z = 2$ for $\text{C}_{36}\text{H}_{54}\text{N}_6(\text{ClO}_4)_2$. The crystallographic data for **2c** are as follows: space group $P2_1$ with $a = 16.121$ (4) Å, $b = 13.218$ (4) Å, $c = 21.703$ (6) Å, $\beta = 108.21$ (2)°, and $Z = 4$ for $\text{C}_{46}\text{H}_{62}\text{N}_6 \cdot 2\text{ClO}_4 \cdot \text{C}_3\text{H}_6\text{O}$. Diffraction intensities were measured by an ω scan technique with a Nicolet P3F autodiffractometer (monochromatized Mo radiation) equipped with a Syntex Lt-1 low-temperature device to maintain crystal temperature at ca. 120 K. For **2a**, 4089 unique data ($2\theta_{\text{max}} \geq 3\sigma(I)$) were collected to a resolution of $2\theta_{\text{max}} = 50^\circ$, and for **2c**, 16383 unique reflections (12731 with $I \geq 3\sigma(I)$) were collected to a resolution of $2\theta_{\text{max}} = 65^\circ$. Three reference reflections, measured periodically, displayed neither systematic nor significant variations in their respective intensities. Data were corrected for Lorentz and polarization effects but not for absorption.

The initial structural models were determined by direct methods¹⁶ and were developed by difference Fourier and least-squares refinement techniques using the XRAY program library.¹⁷ Disorder was encountered in the crystals of both compounds; in **2a** the cation is disordered, while in **2c** the disorder is in the oxygen atoms of the perchlorate anions. In **2a**, the two cation sites were estimated to be equally populated; in **2c**, population of oxygen atoms was estimated from peak heights in difference electron density maps. For **2a**, 3512 reflections contributed to the refinement of 352 variables to give $R = 0.066$ ($R_w = 0.095$), and for **2c**, 14596 reflections contributed to the refinement of 1554 variables to give $R = 0.089$ ($R_w = 0.093$). Atomic coordinates have been deposited.¹⁸

2,2',4,4',6,6'-Hexapyrrolidin-1-yl-1,1'-bicyclohexadienylium Complexes 2. General Methods. The suspension of the 1,3,5-tripyrrolidin-1-ylbenzene **1** (20 mmol) in acetonitrile (60 mL) was gassed for 1 h with dry nitrogen, the reaction vessel was then covered carefully with aluminum foil, and solid silver nitrate (3.4 g, 20 mmol) was added at once in darkness to the stirred suspension at 0 °C. After an additional 15 min at 0 °C under nitrogen atmosphere, workup was done very quickly. The precipitated elemental silver was filtered off, and ether (200 mL) was added to the dark red filtrate. The resulting red oil was dissolved in

water (200 mL), separated from the ethereal phase, and quickly filtered twice. A saturated solution of sodium perchlorate, sodium tetrafluoroborate, or potassium hexafluorophosphate, respectively, was immediately added dropwise to the stirred aqueous filtrate, and the resulting red precipitate was isolated, washed with ether, and dried in high vacuum at 60 °C.

2,2',4,4',6,6'-Hexapyrrolidin-1-yl-1,1'-bicyclohexadienylium Diperchlorate (2a). 1,3,5-Tripyrrolidin-1-ylbenzene (**1a**)¹⁹ (5.7 g) was converted to **2a** (6.75 g, 86%), mp 256 °C. Anal. Calcd for $\text{C}_{36}\text{H}_{54}\text{N}_6(\text{ClO}_4)_2$: C, 56.16; H, 7.07; Cl, 9.21; N, 10.91. Found: C, 56.23; H, 7.36; Cl, 9.41; N, 10.77.

2,2',4,4',6,6'-Hexapyrrolidin-1-yl-1,1'-bicyclohexadienylium Bis(tetrafluoroborate) (2a'). Compound **1a** (5.7 g) was converted to **2a'** (6.5 g, 88%), mp 255 °C. Anal. Calcd for $\text{C}_{36}\text{H}_{54}\text{N}_6(\text{BF}_4)_2$: C, 58.05; H, 7.31; N, 11.26. Found: C, 57.59; H, 7.50; N, 11.10.

3,3'-Dimethyl-2,2',4,4',6,6'-hexapyrrolidin-1-yl-1,1'-bicyclohexadienylium Diperchlorate (2b). 2-Methyl-1,3,5-tripyrrolidin-1-ylbenzene (**1b**)²⁰ (5.9 g) was converted to a red crystalline mixture of the perchlorates **2b** and **3b** (yield 84% by ^1H NMR), which was washed with cold 4:1 methanol/water (50 mL). The residue immediately was dried in high vacuum at 60 °C, yielding **2b** (1.65 g, 20%), mp 165–166 °C. Anal. Calcd for $\text{C}_{38}\text{H}_{58}\text{N}_6(\text{ClO}_4)_2$: C, 57.20; H, 7.32; Cl, 8.89; N, 10.53. Found: C, 57.09; H, 7.24; Cl, 9.08; N, 10.51.

3,3'-Dimethyl-2,2',4,4',6,6'-hexapyrrolidin-1-yl-1,1'-bicyclohexadienylium bis(tetrafluoroborate) (2b') gave analogous results, mp 145 °C. Anal. Calcd for $\text{C}_{38}\text{H}_{58}\text{N}_6(\text{BF}_4)_2$: C, 59.00; H, 7.55; N, 10.64. Found: C, 58.79; H, 7.73; N, 10.48.

3,3'-Diethyl-2,2',4,4',6,6'-hexapyrrolidin-1-yl-1,1'-bicyclohexadienylium Diperchlorate (2c). Acetonitrile (80 mL), dropped through a glass column (packed with Al_2O_3 alumina Woelm B or N-Super I, respectively) into a two-necked flask, was gassed with dry nitrogen. After addition of 2-ethyl-1,3,5-tripyrrolidin-1-ylbenzene (**1c**)²⁰ (5.9 g, 19 mmol), the resulting suspension was stirred for 90 min at 0 °C under nitrogen, and the reaction vessel was then covered carefully with aluminum foil. Solid silver nitrate (3.22 g, 19 mmol) was added, and after an additional 15 min at 0 °C under nitrogen atmosphere, workup was done by the general method (using demineralized water) to give **2c** (7.2 g, 92%), mp 140–144 °C. Anal. Calcd for $\text{C}_{40}\text{H}_{62}\text{N}_6(\text{ClO}_4)_2$: C, 58.17; H, 7.57; Cl, 8.58; N, 10.18. Found: C, 57.36; H, 7.35; Cl, 8.38; N, 9.70.

3,3'-Diethyl-2,2',4,4',6,6'-hexapyrrolidin-1-yl-1,1'-bicyclohexadienylium Bis(hexafluorophosphate) (2c''). Compound **1c** (3.18 g, 10 mmol) in acetonitrile (50 mL) was converted to **2c''** as described above for **2c**, with silver nitrate (1.7 g, 10 mmol) and workup with ether (150 mL), water (150 mL) and a solution of 5.72 g of potassium hexafluoroborate in water/methanol, resulting in 3.32 g (73%), mp 150–152 °C. Anal. Calcd for $\text{C}_{40}\text{H}_{62}\text{N}_6(\text{PF}_6)_2$:

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C, 52.40; H, 6.82; N, 9.17. Found: C, 50.58; H, 6.54; N, 8.86.

3,3'-Diisopropyl-2,2',4,4',6,6'-hexapyrrolidin-1-yl-1,1'-bicyclohexadienylium Diperchlorate (2d). 2-Isopropyl-1,3,5-tripyrrolidin-1-ylbenzene (**1d**)²⁰ (6.55 g) was converted to a red-colored crystalline mixture of **2d** and **3d** (yield 91% by ¹H NMR) as described above for **2b**. Purification of the mixture as described for **2b** afforded **2d** (3.2 g, 36%), mp 124–125 °C. Anal. Calcd for C₄₂H₆₆N₆(ClO₄)₂: C, 59.07; H, 7.79; Cl, 8.30; N, 9.83. Found: C, 59.23; H, 7.69; Cl, 8.37; N, 9.64.

3,3'-Diisopropyl-2,2',4,4',6,6'-hexapyrrolidin-1-yl-1,1'-bicyclohexadienylium bis(tetrafluoroborate) (2d') gave analogous results, mp 125 °C. Anal. Calcd for C₄₂H₆₆N₆(BF₄)₂: C, 60.90; H, 8.03; N, 10.15. Found: C, 61.15; H, 8.13; N, 9.11.

3,3'-Dibutyl-2,2',4,4',6,6'-hexapyrrolidin-1-yl-1,1'-bicyclohexadienylium Diperchlorate (2e). 2-Butyl-1,4,5-tripyrrolidin-1-ylbenzene (**1e**)²⁰ (6.8 g) was converted to a red-colored crystalline mixture of **2e** and **3e** (yield 79% by ¹H NMR) as described above for **2b,d**. Purification of the mixture as described for **2b,d** afforded **2e** (2.4 g, 27%), mp 113–115 °C. Anal. Calcd for C₄₄H₇₀N₆(ClO₄)₂: C, 59.92; H, 8.00; Cl, 8.04; N, 9.53. Found: C, 59.74; H, 7.99; Cl, 8.26; N, 9.62.

2,2',4,4',6,6'-Hexapyrrolidin-1-yl-3,3'-(*o*-phenylenedimethylene)-1,1'-bicyclohexadienylium Diperchlorate (2f). 1,2-Bis(2,4,6-tripyrrolidinobenzyl)benzene (**1f**)²⁰ (12.4 g) was converted to the perchlorate **2f** as described above for **2a** to afford 10.0 g (57%) of red-violet-colored crystals, mp 220 °C. Anal. Calcd for C₄₄H₆₀N₆(ClO₄)₂: C, 60.61; H, 6.93; Cl, 8.13; N, 9.64. Found: C, 60.48; H, 6.85; Cl, 8.04; N, 9.55.

2,2',4,4',6,6'-Hexapyrrolidin-1-yl-1,1'-biphenyls 4. General Methods. The dimeric σ -complex **2** (1 mmol) was dissolved in acetonitrile (30 mL), and the resulting solution was immediately mixed with a solution (10 mL) of sodium methoxide in methanol. Water (150 mL) was added after 30 min, and the mixture was then allowed to stand for 1 h. The light brown precipitate was separated, dried under high vacuum at 60 °C, and recrystallized from acetonitrile (300 mL), yielding colorless crystals.

2,2',4,4',6,6'-Hexapyrrolidin-1-yl-1,1'-biphenyl (4a). Compound **2a** (80 mg) was converted to **4a** (0.505 g, 89%), mp 322–328 °C. Anal. Calcd for C₃₆H₅₂N₆: C, 76.01; H, 9.21; N, 14.77. Found: C, 76.15; H, 9.08; N, 14.84.

3,3'-Dimethyl-2,2',4,4',6,6'-hexapyrrolidin-1-yl-1,1'-biphenyl (4b). Compound **2b** (0.79 g) was converted to **4b** (0.49 g, 82%), mp 180–183 °C. Anal. Calcd for C₃₈H₅₆N₆: C, 74.46; H, 9.46; N, 14.08. Found: C, 76.48; H, 9.36; N, 14.26.

3,3'-Diethyl-2,2',4,4',6,6'-hexapyrrolidin-1-yl-1,1'-biphenyl (4c). Compound **2c** (0.83 g) was converted to **4c** (0.458 g, 73%), mp 162–166 °C. Anal. Calcd for C₄₀H₆₀N₆: C, 76.87; H, 9.68; N, 13.45. Found: C, 76.72; H, 9.57; N, 13.34.

3,3'-Diisopropyl-2,2',4,4',6,6'-hexapyrrolidin-1-yl-1,1'-biphenyl (4d). A saturated solution of potassium hydroxide in water (20 mL) was added to a solution of **2d** (854 mg) in dimethylformamide. The dark red solution decolorized within 1 min. Water (80 mL) was added, and the colorless precipitate was separated by filtration, washed with water, and dried under high vacuum (P₂O₅), yielding 470 mg of **4d** (72%), mp 170–190 °C. After recrystallization of 300 mg from acetonitrile, colorless crystals of **4d** (220 mg, \approx 33%) resulted, mp 201–204 °C. Anal. Calcd for C₄₂H₆₄N₆: C, 77.25; H, 9.88; N, 12.86. Found: C, 77.14; H, 9.79; N, 12.61.

Ethyl 2,4,6-Tripyrrolidin-1-ylbenzyl Ether (6). Ethyl iodomethyl ether (**7**) (11.16 g, 60 mmol) was dropped into a suspension of **1a** (17.1 g, 60 mmol) in ethanol (30 mL). The mixture was refluxed for 5 min, and the dark red solution was mixed with a solution of sodium ethoxide (2.3 g of sodium in 40 mL of ethanol) at room temperature and cooled to –20 °C. The resulting colorless oil was allowed to crystallize, and the crystals were separated and recrystallized from methanol (60 mL), yielding **6** (8.7 g, 42%): mp 86 °C; ¹H NMR (CDCl₃) δ 5.45 [5.47] (s, 2 H, 3-, 5-H), 4.19 [4.17] (s, 2 H, CH₂OCH₂CH₃). Signals in brackets are for **6**, resulting after addition of sodium ethoxide to the product mixture from oxidation of **1b**. Anal. Calcd for C₂₁H₃₃N₃O: C, 73.43; H, 9.69; N, 12.23. Found: C, 73.63; H, 9.47; N, 12.38.

Reactions of 1,3,5-Tripiperidin-1-ylbenzene (8)¹⁹ and 1,3,5-Trimorpholin-1-ylbenzene (9)¹⁹ with Bromine or Halocyanogen. A. General Procedure with Bromine. A solution of bromine in glacial acetic acid (GAA) was slowly dropped into

a stirred solution of **8** or **9** in GAA at room temperature.

A.1. Compound **8** (3.28 g, 10 mmol) in GAA (60 mL) was treated with Br₂ (1.6 g, 10 mmol) in GAA (20 mL) as described above, and the red solution was then stirred for 4 h at room temperature. After addition of water (400 mL) and alkalization with NaOH, the light colored precipitate was filtered off, washed with water, and dried, yielding 4.1 g of product, mp 265–271 °C dec. Recrystallization of 2 g from acetonitrile gave on cooling of the red solution a brown-colored powder (620 mg), which was filtered off after 1 day. It was treated with ether and filtered off again to afford 1-bromo-2,4,6-tripiperidin-1-ylbenzene hydrobromide (**10-HBr**) (230 mg), mp 260–268 °C, after purification by recrystallization from methanol, mp 278–280 °C. Another light brown residue of **10-HBr** (142 mg, mp 270–275 °C dec) could be separated after concentration and cooling of the acetonitrile filtrate, mp 278–280 °C (methanol). Total yield of **10-HBr** 372 mg, \approx 15%. Anal. Calcd for C₂₁H₃₂BrN₃·HBr: C, 51.74; H, 6.83; Br, 32.79; N, 8.61. Found: C, 51.69; H, 6.84; Br, 32.59; N, 8.56.

The remaining acetonitrile filtrate was evaporated to dryness, leaving a black residue, which was dissolved in hot methanol (10 mL). After gradual addition of ether (200 mL) to the cold solution, red crystals of the dimeric σ -complex **12a** (450 mg, \approx 22% calcd for 2X⁻ = 2Br⁻) were separated after 2 days, mp 265–270 °C dec. A correct analysis for 2,2',4,4',6,6'-hexapiperidin-1-yl-1,1'-bicyclohexadienylium dibromide (**12a**) could not be obtained. Anal. Calcd for C₄₂H₆₆N₆Br₂: C, 61.90; H, 8.16; Br, 19.61; N, 10.30. Found: C, 58.46; H, 7.68; Br, 19.24; N, 9.31.

The ethereal filtrate of the first isolated fraction of **10-HBr** was evaporated to dryness, leaving 1-bromo-2,4,6-tripiperidin-1-ylbenzene (**10**) (380 mg, \approx 19%), mp 130–135 °C, which was purified by recrystallization from acetonitrile to afford colorless crystals, mp 136–137 °C. Anal. Calcd for C₂₁H₃₂BrN₃: C, 62.06; H, 7.94; Br, 19.65; N, 10.35. Found: C, 62.40; H, 7.87; Br, 19.48; N, 10.21.

A.2. Compound **8** (3.28 g) in GAA (60 mL) was treated with bromine (1.6 g) in GAA (20 mL) as described above. After 30 min of stirring at room temperature, a violent stream of gaseous HCl was passed through the solution for 10 min, followed by an additional 3 h of stirring. After addition of water (500 mL) and alkalization with NaOH, the colorless precipitate was filtered off, washed with water, and dried to afford 4.04 g of product, mp 113–114 °C. Recrystallization of 1.2 g from acetonitrile gave **10** (638 mg) as light brown colored powder, mp 128–132 °C, and concentration of the filtrate and cooling afforded another fraction of **10** (166 mg), mp 127–129 °C. Both fractions are purified by recrystallization twice from acetonitrile to give **10**, mp 137–138 °C. Total yield of **10**: 840 mg, \approx 66%. After addition of ether to the remaining acetonitrile filtrate, red crystals of **12a** (39 mg, \approx 3% calcd for 2X⁻ = 2Br⁻) were separated after 3 days, mp 265–270 °C dec.

A.3. Compound **9** (3.33 g, 10 mmol) in GAA (80 mL) was treated with bromine (1.6 g) in GAA (60 mL) as described above, and the dark red solution was stirred for 24 h at room temperature. After addition of water (300 mL) and alkalization with NaOH, the precipitate was filtered off after 2 h, washed with water, and dried. The pink-colored product (2.8 g) was then recrystallized from acetonitrile (100 mL) to afford colorless needles of 1-bromo-2,4,6-trimorpholin-1-ylbenzene (**11**) (1.85 g, 45%), mp 242–244 °C. Anal. Calcd for C₁₈H₂₆BrN₃O₃: C, 52.43; H, 6.35; Br, 19.37; N, 10.18. Found: C, 52.73; H, 6.33; Br, 19.45; N, 9.98.

B. General Procedure with Bromocyanogen. A solution of bromocyanogen (1.06 g, 10 mmol) in ether (25 mL) was dropped into the stirred solution of **8** or **9** (10 mmol) in chloroform at room temperature.

B.1. BrCN in ether was added to **8** (3.28 g) in CHCl₃ (25 mL) within 5 min as described above. Stirring of the red solution was continued for 1 day, and the red crystals of the dimeric σ -complex **12a** (1.5 g, 36% calcd for 2X⁻ = 2Br⁻) were then filtered off, mp 270–275 °C. The filtrate was evaporated to dryness, leaving a light brown residue of **10** (3.0 g, 74%), mp 115–120 °C, which was purified by recrystallization from acetonitrile/activated carbon to give a mp of 138 °C.

B.2. BrCN in ether was added to **9** (3.33 g) in CHCl₃ (80 mL) within 2 min as described above. After an additional 4 days of stirring, the golden-yellow solution was evaporated to dryness, leaving a light brown residue of **11** (4.05 g), which was recrystallized from dimethylformamide/acetonitrile (100 mL) to afford colorless

needles of 11 (2.9 g, 70%), mp 245 °C.

C. Iodination with Iodocyanogen. C.1. A solution of ICN (1.53 g, 10 mmol) in absolute ether (25 mL) was added to the stirred solution of 8 (3.28 g) in absolute chloroform at room temperature. Stirring of the red solution was continued for 5 days, and the red powder was then filtered off, washed with ether, and dried to afford 2,2',4,4',6,6'-hexapiperidin-1-yl-1,1'-bicyclohexadienylum bis(diiodocyanide) (**12b**) (2.52 g, 42%), mp 154-155 °C. Anal. Calcd for $C_{42}H_{86}N_6(I_2CN)_2$: C, 43.50; H, 5.48; I, 41.77; N, 9.22. Found: C, 43.60; H, 5.37; I, 41.71; N, 9.19.

The filtrate was evaporated to dryness, leaving a dark brown residue (2.5 g), mp 135 °C, which was purified by recrystallization twice from *n*-heptane/activated carbon to afford the educt 8, mp and mixed mp 182-184 °C (lit.¹⁹ mp 183-184 °C).

C.2. A solution of ICN (3.06 g, 20 mmol) in absolute ether (50 mL) was dropped into a stirred suspension of 8 (3.28 g) in absolute ether (50 mL) at room temperature. The separated red powder of **12b** was filtered off at several times (after 8 h, 515 mg; after 32 h, 770 mg; after 56 h, 290 mg; and after 4 weeks, 1.85 g). Total yield of **12b**: 3.43 g (56%), mp 152-155 °C.

C.3. A solution of ICN (6.12 g, 40 mmol) in absolute ether (100 mL) was dropped into a stirred solution of 9 (6.66 g, 20 mmol) in absolute chloroform (250 mL) at room temperature. After an additional 3 days of stirring of the dark brown solution, the resulting brown powder of the dimeric σ -complex **13** (60 mg), mp 120-125 °C, was filtered off. Further fractions of red-brown-colored product were filtered off within 2 weeks in periods of several days; total yield, 240 mg. The melting points of these fractions increased continuously to 140-145 °C (fourth and fifth fractions)—obviously the anion of the σ -complex **13** changed, e.g., to CN^- , I_2CN^- , and I_3^- , respectively. Anal. Calcd for 2,2',4,4',6,6'-hexamorpholin-1-yl-1,1'-bicyclohexadienylum bis(triiodide) (**13d**) $C_{36}H_{54}N_6O_6(I_3)_2$ (fifth fraction): C, 30.28; H, 3.81; N, 5.87. Found: C, 30.43; H, 3.87; N, 5.75. The filtrate was evaporated to dryness, leaving a brown-colored powder (9.2 g), mp 170 °C. Recrystallization of 4.2 g from dimethylformamide/acetone (1:1) afforded 9 as light yellow colored product, which was filtered off, washed with methanol and ether, and dried, yielding 1.2 g, mp 310-315 °C (lit.¹⁹ mp 308-312 °C).

Reactions of the Dimeric σ -Complexes 12 and 13. 2,2',4,4',6,6'-Hexapiperidin-1-yl-1,1'-bicyclohexadienylum Diperchlorate (**12c**). A solution of 10% aqueous sodium perchlorate (40 mL) was added to a shaken solution of **12a** (1.0 g) in water (100 mL). The precipitated yellow-colored product (0.81 g), mp 210-212 °C, was filtered off after 1 h, washed with water, dissolved in dimethylformamide (17 mL), treated with activated

carbon, and filtered. Ether (50 mL) was then slowly added to the filtrate, yielding the diperchlorate **12c** as fiery-red-colored product (0.77 g), which was separated by filtration and recrystallized again from dimethylformamide/ether to afford **12c**, mp 215-216 °C. Anal. Calcd for $C_{42}H_{86}N_6(ClO_4)_2$: C, 59.07; H, 7.79; Cl, 8.31; N, 9.84. Found: C, 58.97; H, 7.75; Cl, 8.48; N, 9.93.

2,2',4,4',6,6'-Hexapiperidin-1-yl-1,1'-biphenyl (**14**). A solution of sodium hydroxide (1.5 g) in water (15 mL) was added to a shaken solution of **12a** (163 mg) in water (20 mL). The resulting precipitate of colorless **14** was separated by filtration after 30 min, washed with water, and dried, to give 130 mg, mp 270-310 °C. The product was purified by recrystallization twice from dimethylformamide, yielding a mp of 319-321 °C. Anal. Calcd for $C_{42}H_{64}N_6$: C, 77.25; H, 9.88; N, 12.87. Found: C, 77.27; H, 9.83; N, 12.86.

B. A solution of 5% aqueous NaOH (2 mL) was dropped into a shaken solution of diperchlorate **12c** (342 mg) in dimethylformamide (10 mL). Water (100 mL) was added after 30 min, and the resulting precipitate of **14** was filtered off, washed with water, and dried, yielding 205 mg (78%), mp 310-315 °C, which was recrystallized from dimethylformamide to afford a mp and mixed mp of 319-320 °C.

C. A solution of 5% aqueous NaOH (20 mL) was added to a filtered and shaken solution of bis(diiodocyanide) **12b** (2.1 g) in dimethylformamide (80 mL). The resulting precipitate, separated by filtration after 1 h (0.99 g, mp 285-320 °C) and recrystallized from dimethylformamide, was identified as **14**, mp and mixed mp 320-322 °C.

2,2',4,4',6,6'-Hexamorpholin-1-yl-1,1'-biphenyl (**15**). A solution of 5% aqueous NaOH (15 mL) was added to a shaken solution of the bis(triiodide) **13d** (200 mg) in dimethylformamide (10 mL). The resulting colorless precipitate of **15** (84 mg) was recrystallized from dimethylformamide (2 mL), yielding colorless crystals of **15**, mp 344-346 °C. Anal. Calcd for $C_{36}H_{52}N_6O_6$: C, 65.02; H, 7.88; N, 12.65. Found: C, 64.89; H, 7.80; N, 12.62.

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Supplementary Material Available: Fractional atomic coordinates, anisotropic temperature factors for non-hydrogen atoms, fractional atomic coordinates, and isotropic temperature factors for H atoms for **2a** and **2c** and a summary of bonding parameters for **2c** (16 pages). Ordering information is given on any current masthead page.

Twisting in the Tetraphenylethylene Dianion

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The dipotassium salt of the tetraphenylethylene dianion (1^{2-}) has been studied by 1H and ^{13}C NMR spectroscopy and π -MO calculational techniques. Analysis of one-bond and three-bond carbon-carbon coupling constants permits a description of the geometry of the contact ion pair of 1^{2-} . We find a linear relationship between π bond order and carbon-carbon coupling constants, which provides information concerning the torsional angles about those bonds. The preferred geometry of 1^{2-} is one in which the $C_{\alpha}-C_{\alpha'}$ torsional angle is closer to the $C_{\alpha}-C_{\alpha'}$ torsional angle of neutral **1** than to 90°, with the estimated range of this torsional angle being 8.4-28°.

Control of redox reactivity requires a secure chemical basis for discriminating between single and multiple electron transfer. Although the problem can be approached thermally by employing differentially electronically populated transition metal complexes, we sought to find redox catalysts that could be activated photochemically to induce selective two-electron transfer.

In that vein, we were attracted to tetraarylethylenes, a family that included several members known to be reduced electrochemically via two-electron transitions. The conventional explanation involves an overpotential for attachment of the first electron caused by a required geometry change. That is, the radical anion formed by adding a single electron was thought to have twisted slightly from