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2,6,10-Tris(dialkylamino)trioxatriangulenium Ions. Synthesis, Structure, and Properties of Exceptionally Stable Carbenium Ions

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Abstract: A general synthetic route to a novel type of triamino-substituted planar carbenium ions (**5**) is reported. The synthetic method is based on a facile and selective nucleophilic aromatic substitution on the tris(2,4,6-trimethoxyphenyl)carbenium ion (**1**) with amines and gives access to a wide variety of more complex amino-substituted carbenium ions. X-ray crystallography shows that the 2,6,10-tris(*N*-pyrrolidinyl)-4,8,12-trioxatriangulenium ion (**5b**) is planar and forms segregated stacks of cations and PF_6 anions in the solid phase. The stability of the 2,6,10-tris(diethylamino)-4,8,12-trioxatriangulenium ion **5a** is expressed as the pK_{R+} value, which is determined in strongly basic nonaqueous solution on the basis of a new acidity function $C\_$. The pK_{R+} value of **5a** is measured to be 19.7, which is 10 orders of magnitude higher than the values found for the most stable carbenium ions previously reported. Electrochemical reduction of compound **5a** leads to rapid dimerization. Two consecutive one-electron oxidations are identified by cyclic voltammetry.

Introduction

Stabilized carbenium ions such as the triarylmethyl and xanthyl cations are organic compounds of great scientific and commercial importance. Many of them are used as textile dyes despite their low lightfastness, whereas others serve as laser dyes. Consequently, their photophysical properties have been extensively studied.[1]

Crystal violet (CV) and the trioxatriangulenium[2] cation (TOTA) (Figure 1) are among the most stable carbenium ions. The two carbenium ions show almost the same pK_{R+} value, $pK_{R+} = 9.36$[3] and 9.05,[4] respectively. The pK_{R+} value expresses the reactivity of the cation toward hydroxide ions.[5] The high stability of the CV cation can be explained by the strong electron-donating ability of the three dimethylamino substituents, which by simple resonance delocalize the charge. Good correlation between the electron-donor strength (σ^+) of the *para* substituents and the pK_{R+} value is found for substituted triarylcarbenium ions.[6−8] A similar correlation is found between the ^{13}C chemical shift values of the central carbon atoms, the calculated charge density and σ^+.[9] Thus, among the triarylcarbenium ions, the pK_{R+} value can be taken as a measure of the charge density at the central carbon atom.

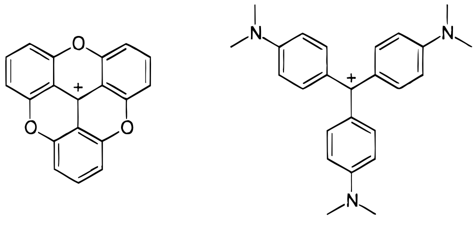

Figure 1.

When comparing with other carbenium ions such as the tris-(4-methoxyphenyl)carbenium ion ($pK_{R+} = 0.82$), it becomes obvious that the high stability of the TOTA cation does not rely merely on the presence of the three oxygen atoms but also on the complete planarity of the molecular framework[10] which allows substantial delocalization of the positive charge. The reversible reaction with hydroxide ions (defining the pK_{R+} value) becomes even further unfavorable due to destabilization of the corresponding carbinol by internal strain when the central carbon is forced into sp^3 hybridization.[11]

We report a general synthetic scheme leading to the novel 2,6,10-tris(dialkylamino)-4,8,12-trioxatriangulenium system **5** and results from the investigations of its structure and physicochemical properties.

The tris(dialkylamino)trioxatriangulenium system was designed and prepared as part of our ongoing quest for highly

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(1) Duxbury, D. F. *Chem. Rev.* **1993**, *93*, 381−433.

(2) We have chosen to use the trivial name trioxatriangulene in line with the names used for other derivatives[10,59−64] of the analogous hydrocarbon triangulene.[65] The systematic name of the TOTA system is 4,8,12-trioxa-4,8,12,*12c*-tetrahydrodibenzo[*cd*,*mn*]pyrene.

(3) Goldacre, R. J.; Phillips, J. N. *J. Chem. Soc.* **1949**, 1724−1732.

(4) Martin, J. C.; Smith, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 2252−2256.

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(10) Krebs, F. C.; Laursen, B. W.; Johansen, I.; Boubekeur, K.; Bechgaard, K.; Jacobsen, C. S.; Faldt, A.; Thorup, N. *Acta Crystallogr., Sect. B*, in press.

(11) For a discussion of steric and strain effects in related systems, see ref 5.

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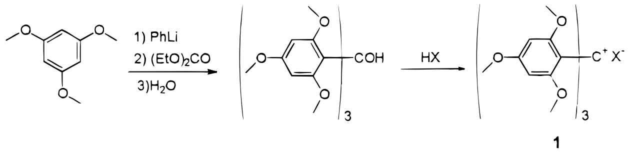
Scheme 1[a]



[a] $X = Cl^-$ or BF_4^-.

stable, planar carbenium ions with the potential to form segregated stacks of cations and anions.

Results and Discussion

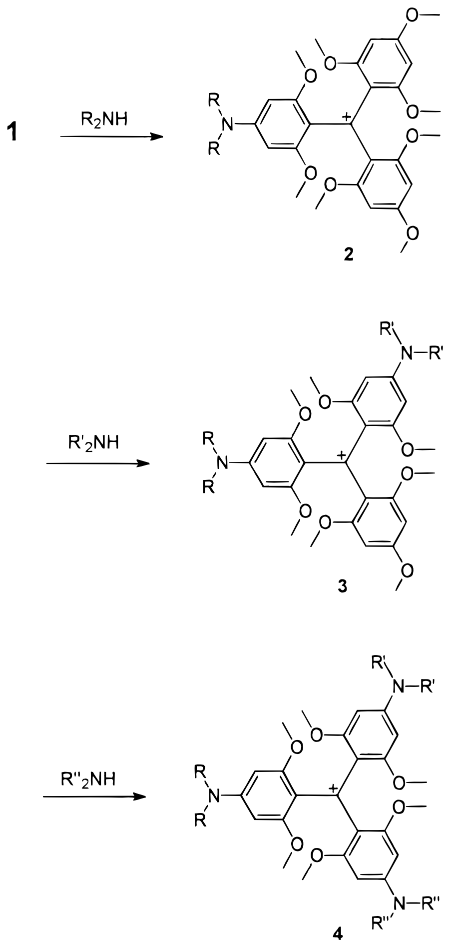
Synthesis. The synthetic procedures leading to trioxatriangulenium systems are few in the literature. The only derivative described is tri-*tert*-butyltrioxatriangulenium hexafluorophosphate,[12] which was synthesized by the same method as originally applied to the unsubstituted system,[4] using 1,3-dimethoxy-5-*tert*-butylbenzene as the starting material. Lofthagen et al.[13-15] have prepared and used several derivatives of the nonionic *12c*-methylated triaminotrioxatriangulene system in their work with macrocyclophanes.

The synthetic approach used in the present work is based on a facile nucleophilic substitution of *p*-methoxy and *p*-chloro substituents in triaryl carbenium ions.[16-19] We have synthesized the novel[20] tris(2,4,6-trimethoxyphenyl)carbenium ion (**1**) (Scheme 1) by a method analogous to the one used by Martin and Smith in their synthesis of tris(2,6-dimethoxyphenyl)carbinol.[4] Compound **1** is obtained in one step as the tetrafluoroborate or chloride salt by addition of the corresponding acids directly to the hydrolyzed reaction mixture containing the carbinol. This one-step reaction was performed on a multigram scale, yielding as much as 26 g of the crude **1** (96% yield), which was used without further purification in the subsequent reactions.

The *p*-methoxy groups in compound **1** undergo aromatic nucleophilic substitution (S_NAr) with dialkylamines as outlined in Scheme 2. By controlling the reaction conditions, it is possible to obtain products in which one, two, or three of the *p*-methoxy groups of compound **1** are substituted. During the stepwise reaction, it is possible to replace the remaining methoxy groups with a different dialkylamine without affecting the amino group already introduced. This synthetic strategy permits the preparation of a wide variety of amino-substituted carbenium ions from one single precursor (**1**).

Nucleophilic Substitution. The S_NAr reaction with dialkylamines is carried out in polar solvents such as DMF or acetonitrile at room temperature using the crude BF_4^- or Cl^- salts of compound **1**. A significant decrease in reactivity following each consecutive substitution is observed. Thus, to substitute all three *p*-methoxy groups of compound **1**, it is necessary to use a large excess of amine and long reaction times.

Scheme 2[a]



[a] **a**: R = R′ = R″ = Et. **b**: R = R′ = R″ = *N*-pyrrolidinyl. **c**: R = Et, R′ = R″ = *N*-morpholinyl. **d**: R = R′ = R″ = *N*-morpholinyl.

Two symmetrically amino-substituted carbenium ions were obtained in one-pot reactions of compound **1** with a large excess of diethylamine or pyrrolidine, leading to compounds **4a** and **4b**, respectively (Scheme 2). The observed decrease in reactivity in the subsequent S_NAr reactions of **1** can be rationalized in terms of the increasing delocalization of the positive charge as the *p*-methoxy groups are exchanged by the stronger electron-donating amino groups, whereby the electrophilicity of the remaining unsubstituted *para* positions is reduced. The decreasing order of reactivity observed when going from compound **1** to **3** (Scheme 2) makes selective synthesis of the partially substituted compounds **2** and **3** possible. Thus, compound **2a** was obtained in 76% yield by the addition of 4 equiv of diethylamine to **1** and quenching the reaction after only 5 min, whereas compound **3a** was obtained in 78% yield after **1** had reacted with excess diethylamine for 20 h. Asymmetrically substituted compounds can also be prepared. Thus, compound **4c** was obtained when compound **2a** was allowed to react with a large excess of the strong nucleophile morpholine for 24 h. The asymmetric triamino compound **4c** was isolated in 85% yield, and only traces of a tris(*N*-morpholinyl) compound **4d** were observed.[21] These results clearly indicate that the introduction of amino groups in compound **1** is practically irreversible under the reaction conditions applied.

The successful implementation of the S_NAr reactions to these carbenium ions, under conditions where a large excess of amine

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[20] During the preparation of this manuscript, Wada et al. published a synthesis of the corresponding carbinol and its perchlorate salt; see ref 66.

[21] In the FABMS spectra, the intensity of the $m/z = 664$ peak (**4d**) in the raw product was less than 2% of the $m/z = 678$ peak (**4c**).

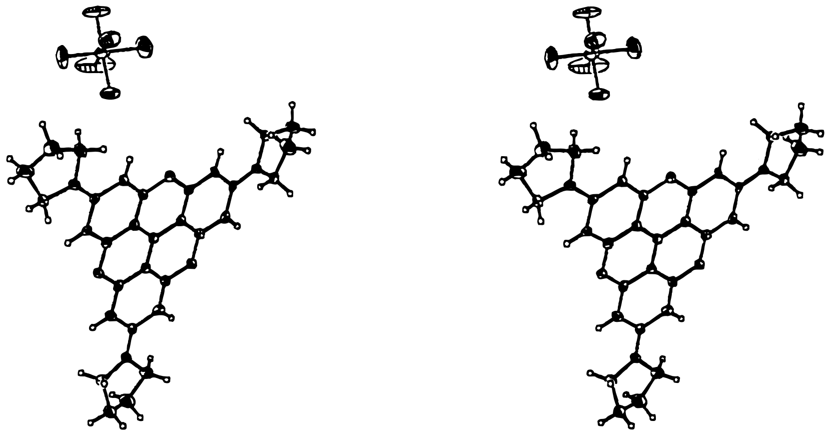
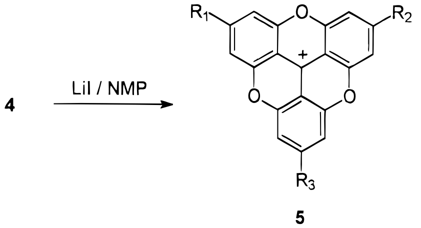


Figure 2. ORTEP drawing of **5b-PF$_6$**, stereoview.

Scheme 3[a]



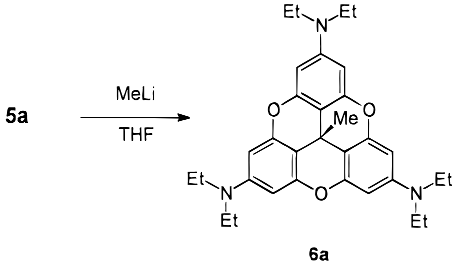
[a] **5a**: R$_1$ = R$_2$ = R$_3$ = NEt$_2$. **5b**: R$_1$ = R$_2$ = R$_3$ = *N*-pyrrolidinyl. **5c**: R$_1$ = NEt$_2$, R$_2$ = R$_3$ = *N*-morpholinyl.

is present, rely on the presence of the six *o*-methoxy groups that surround and shield the cationic center,[22] thus preventing a nucleophilic attack on the central carbon.

Ring Closure. The ring closure of compounds **4a**−**c** to the corresponding tris(dialkylamino)trioxatriangulenium ions **5a**−**c** was performed by heating with LiI in NMP (Scheme 3). The use of LiI as a reagent for dealkylation of methylaryl ethers is well known.[23,24] However, to our knowledge, it has not previously been used to promote the present type of ring closure. LiI was selected after several attempts with other reagents. Thus, attempts to perform the ring closure of **4a** in molten pyridine hydrochloride at 180 °C, in analogy with the preparation of TOTA,[4] resulted in a high degree of N-dealkylation along with ring closure. The same result was obtained upon heating **4a** in polyphosphoric acid. The facile N-dealkylation of **4a** and **5a** under these conditions is in accordance with the findings of Chambers and Pearson.[25] Also, a purely thermolytic, uncatalyzed ring closure[26] was attempted by refluxing **4a** in high-boiling solvents such as DMSO and NMP. This procedure gave the desired product (**5a**) but at a very low rate. Partially ring-closed compounds were the main products even after prolonged heating.

Alkylation. As previously mentioned, *12c*-methylated derivatives of compound **5** have been used in the preparation of several macrocyclophanes. These compounds were synthesized by methylation in the *12c* position of the TOTA cation followed by bromination and cine substitution.[15] Alkylation at the *12c* position of compound **5** would offer an alternative route to these compounds. The TOTA cation has been alkylated with alkyllithium[15] and alkyl copper[12] reagents. In our hands, methylation of compound **5a** with methyllithium in THF gave the *12c*-methylated compound **6a** in 80% yield (Scheme 4).

Scheme 4



Molecular and Crystal Structure. All tris(dialkylamino)-trioxatriangulenium salts investigated form needle-shaped orange crystals. However, X-ray data of sufficient quality for structure determination could only be obtained for the PF$_6^-$ salt of the tris(*N*-pyrrolidinyl) derivative (**5b**). Crystals of **5b-PF$_6$** were grown from dichloromethane/ethyl acetate solution by slow evaporation. The structure was solved and refined in the space group *P*2(1)/*n* with four molecules per unit cell. The molecular structure of the cation shows the expected quasi-D_{3h} symmetry with the three nitrogens in the plane of the molecule (Figure 2). The configuration around the three nitrogens is planar, with an average sum of the bond angles of 359.3(1)°. The length of the bond connecting the nitrogens with the aromatic system is only 1.344(7) Å, indicating a strong interaction and some double bond character between the nitrogens and the trioxatriangulenium system. Thus, it is expected that a considerable amount of the positive charge is localized on the three nitrogen atoms. This charge distribution is also in accordance with the packing of the ions, since the cations form segregated stacks surrounded by stacks of hexafluorophosphate ions in a pseudohexagonal pattern (Figure 3), that is, the anions are located in proximity of the amino groups rather than the central carbon. The cations are packed in a staggered arrangement with a repetition distance of 8.39 Å and an interplanar distance of only 3.32 Å (Figure 4). The close packing of the cations further stresses the high degree of charge delocalization. Comparable interplanar distances are found in the conducting fluoranthenyl radical cation salts.[27,28] The cations in **5b-PF$_6$** are tilted 37.55° with respect

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[22] The X-ray structure of a similar carbenium ion is found in ref 67. The low reactivity of the cationic center in analogous carbenium ions are discussed in refs 66 and 68.

[23] Harrison, I. T. *Chem. Commun.* **1969**, 616.

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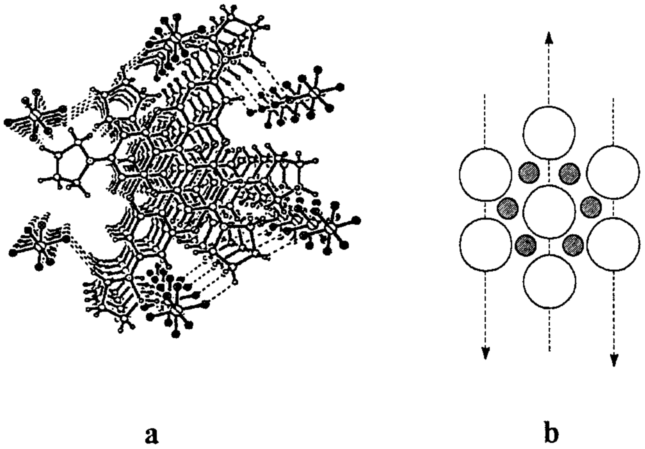


Figure 3. (a) View along the *b*-axis. For clarity the pyrrolidinyl groups on one side of the stack are omitted, except in the top layer. (b) Schematic representation of the pseudohexagonal packing of the stacks of cations and anions. Arrows indicate the tilting direction.

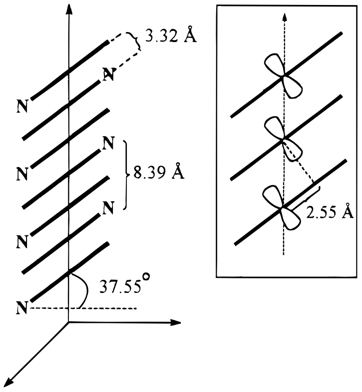


Figure 4. Side view of a stack of planar carbenium ions (**5b-PF$_6$**).

to the stacking axis (the *b*-axis). This causes a 2.55-Å displacement of the central carbon atom relative to its nearest neighbor (Figure 4). The packing pattern is in contrast to the packing patterns of the TOTA salts previously investigated,[10] where the anion is located near the central carbon atom. These fundamental differences in the packing patterns illustrate the importance of the amino groups in terms of charge distribution.

Stability of the Carbenium Ions. The affinity of the carbenium ion toward hydroxide ions, expressed by the pK_{R+} value, is the most common measure of carbenium ion stability.[5] The pK_{R+} parameter is defined in eq 1.

$$\mathrm{p}K_{R+} = H_x + \log \frac{[R^+]}{[ROH]} \qquad (1)$$

H_x is an acidity function characteristic for the carbenium/carbinol equilibrium and the solvent system. In water, H_x is identical to the normal pH scale. A pK_{R+} value of 9.05, as has been reported for TOTA,[4] implies that the carbenium ion is 50% converted to its carbinol at pH = 9.05.

To elucidate the degree of charge delocalization in the tris(dialkylamino)trioxatriangulenium ion (**5**) relative to related compounds such as CV and TOTA, we decided to determine the pK_{R+} value of **5a**. However, observation of the equilibrium between **5a** and the corresponding carbinol **7a** (Scheme 5) is not possible in aqueous solution because the carbinol is not formed in measurable quantities even in 2 M KOH.

There are several examples in the literature of pK_{R+} measurements in nonaqueous solution by use of the C_0 function[29] (also known as the H_R function[5]). These studies, however, deal with unstable carbenium ions generated in solutions more acidic than water. As no investigations of the carbenium/carbinol equilibrium in strongly basic solvent systems have been reported, a new acidity function had to be established. A solvent system consisting of varying proportions of DMSO and water with a constant concentration of tetrabutylammonium hydroxide (Bu$_4$NOH) was chosen. This solvent system was also used by Dolman and Stewart for the construction of an $H\_$ acidity function based on the deprotonation of substituted anilines and diphenylamines.[30] The $H\_$ acidity function is an extension of the pH scale into solutions more basic than can be obtained in water. In the DMSO/water/Bu$_4$NOH solvent system, the basicity (the activity of the hydroxide ion as a proton acceptor) is changing with the DMSO/water ratio, each ratio corresponding to a specific $H\_$ value.

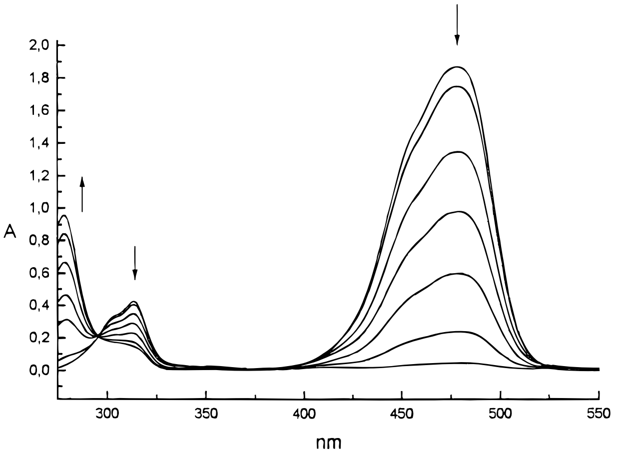
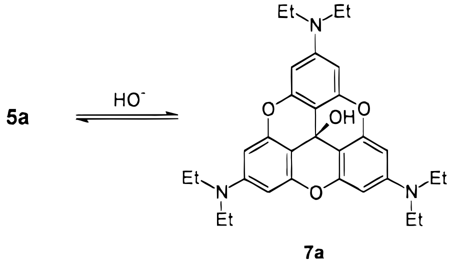


Figure 5. Absorption spectra of **5a**/**7a** in the DMSO/water/Bu$_4$NOH solvent system. Arrows indicate the change from **5a** to **7a** with increasing mol % DMSO. An isosbestic point is observed at 296 nm, indicating the absence of other equilibria.

Scheme 5



The relative concentrations of **5a** and the corresponding carbinol **7a** were measured in the DMSO/water/Bu$_4$NOH system by means of absorption spectroscopy (see Experimental Section). Figure 5 shows the change in absorption of **5a** as the molar percentage of DMSO increases. At 56.5 mol % DMSO, the cation is 50% converted to the carbinol.[31] A logarithmic plot of the carbinol/carbenium ratio (K) versus the $H\_$ value in the range of 40−70 mol % DMSO shows a linear relationship with a slope of 1.31 (Figure 6). The linearity of the plot indicates that the carbenium/carbinol equilibrium responds in the same way to change in the DMSO mol % as do the amines, which were used to construct the $H\_$ function.[30] A slope greater than one indicates a higher susceptibility in the case of the carbenium/

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[29] Deno, N. C.; Jaruzelski, J. J.; Schriesheim, A. *J. Am. Chem. Soc.* **1955**, *77*, 3044−3051.

[30] Dolman, D.; Stewart, R. *Can. J. Chem.* **1967**, *45*, 911−924.

[31] The carbinol (**7a**) was identified by NMR spectroscopy. Chemical shift values are given in the Experimental Section.

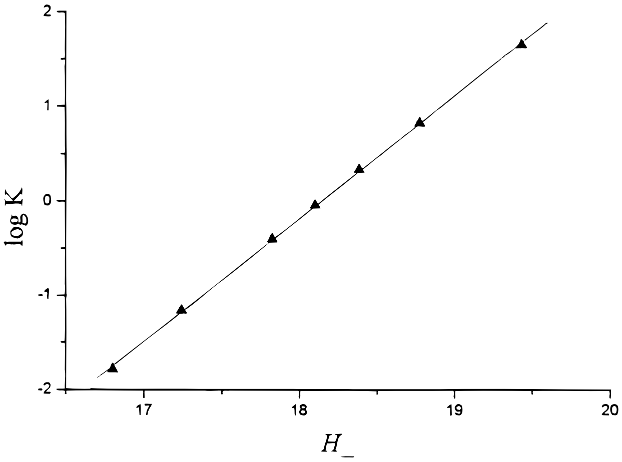
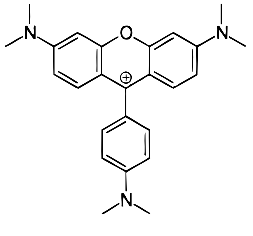


Figure 6. Linear fit to log *K* vs *H*_ for compound **5a**.



OCV

Figure 7.

carbinol reaction than that observed for deprotonation of the amines. To further investigate the relation between the carbenium ion/carbinol equilibrium and the $H\_$ function, the equilibrium distribution between 9-(4-dimethylaminophenyl)-3,6-bis(dimethylamino)xantenium ion (OCV, Figure 7) and its carbinol was determined in the DMSO/water/Bu_4NOH system. In the range of 10−20 mol % DMSO, OCV shows the same behavior as **5a** with a slope of 1.30 for the linear plot of log K vs $H\_$. On the basis of these findings, we believe that this relationship is general, at least up to 70 mol % DMSO. Using the $\mathrm{p}K_{\mathrm{R+}}$ value of OCV (determined in aqueous solution, $\mathrm{p}K_{\mathrm{R+}} = 13.51$), we have constructed a new acidity function $C\_$[32] to be used in the determination of $\mathrm{p}K_{\mathrm{R+}}$ values of highly stabilized carbenium ions in the DMSO/water/Bu_4NOH solvent system. The $C\_$ function was obtained by modifying Dolman and Stewart's $H\_$ function, so that the slope of the straight-line plots of log K vs mol % DMSO for **5a** and OCV becomes unity (eq 2).

$$\mathrm{d}C\_ = 1.31\,\mathrm{d}H\_ \qquad (2)$$

The relationship between the two acidity functions $H\_$ and $C\_$ is illustrated in Figure 8. The higher susceptibility of the carbenium/carbinol equilibrium relative to deprotonation is analogous to the relationship between the C_0 (H_R) function and the H_0 acidity function.[33,34] The deviations between $C\_$ and $H\_$ are most likely related to the very different solvation of the reactants and products in the two defining reactions (the deprotonation reactions defining the $H\_$ function and the hydroxylation of carbenium ions defining the $C\_$ function).

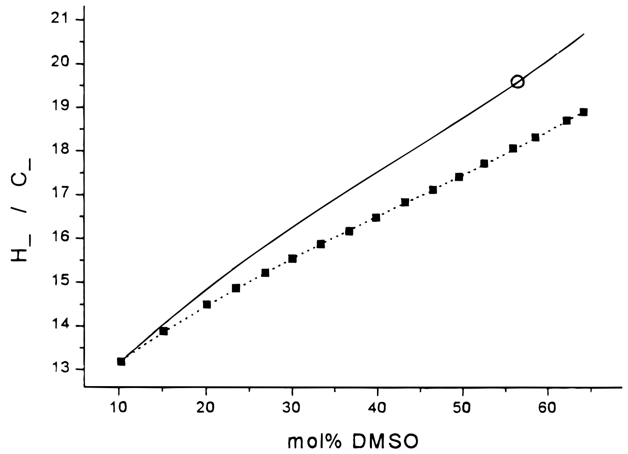


Figure 8. Third-order polynomium (···) fitted to Dolman and Stewart's data (■). The $C\_$ function is shown as a solid line. The position of log $K = 0$ for **5a**/**7a** is indicated by ○.

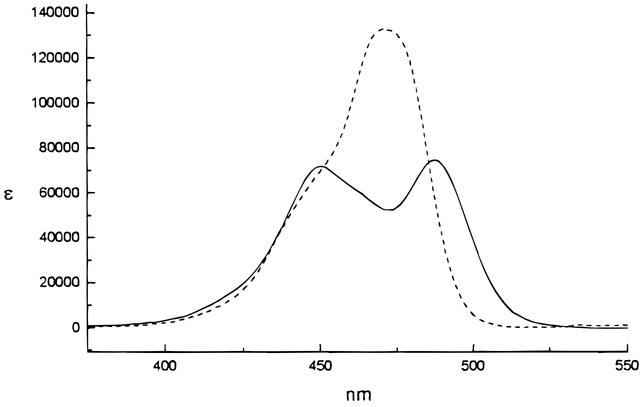


Figure 9. Absorption spectra of **5a-PF₆** (2.85×10^{-6} M) in benzene (—) and dichloromethane (− − −).

Applying the $C\_$ function, the $\mathrm{p}K_{\mathrm{R+}}$ value of **5a** becomes 19.7, which is 10 orders of magnitude higher than those for the most stable carbenium ions previously reported (CV[3] and TOTA[4]). It is 6 orders of magnitude higher than that for the OCV ion, determined in this study.

It should be stressed that the validity of the $C\_$ function is based entirely on the assumption of proportionality between the slopes of the $H\_$ and $C\_$ functions (eq 2). At the present time only two compounds (**5a** and OCV) have been investigated and found to support this hypothesis. Further validation of the $C\_$ function requires that other carbenium ions with $\mathrm{p}K_{\mathrm{R+}}$ values in the range from 13 to 18 are synthesized and their $\mathrm{p}K_{\mathrm{R+}}$ values are determined. This work is in progress.

Electronic Absorption Spectra. The absorption spectrum of compound **5a** in dichloromethane (Figure 9) shows a very intense absorption in the visible region ($\lambda_{\max} = 471$ nm, $\epsilon = 132\,000$ $\mathrm{M^{-1}\,cm^{-1}}$) with a shoulder at the high-energy side of the band. The shape and intensity of this absorption resembles the characteristic spectra of CV and related compounds.[35] Relative to CV ($\lambda_{\max} = 586$ nm, $\epsilon = 115\,000$ $\mathrm{M^{-1}\,cm^{-1}}$),[36] the low-energy absorption of **5a** is blue-shifted by approximately 4200 $\mathrm{cm^{-1}}$ and is more intense. These observations are in agreement with previous studies of the relationship between structure and excitation energy in triphenylmethane dyes. A hypsochromic shift is expected as a consequence of the forced

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[32] The notation $C\_$ was chosen since this acidity function expresses the change in activities of HO^- toward carbenium ions, just as the $H\_$ acidity function is a measure of the HO^- activity toward acidic protons.

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planarity of the molecule[37,38] and the introduction of the electron-donating substituents in the *ortho* positions of the phenyl groups.[39]

In benzene, the absorption spectrum of **5a** (Figure 9) is clearly different because the two closely overlapping transitions in dichloromethane become well resolved. This behavior is also observed in the spectra of CV and related compounds,[35,40−44] and has been the subject of much debate. The latest investigations[35,41,44] provide strong evidence for an interpretation of the phenomena in terms of the formation of a tight ion pair in nonpolar solvents. In dichloromethane solution, the cation **5a** is solvated symmetrically and the molecule maintains its fundamental D_{3h} symmetry (D_3 for CV). Therefore, the S_1 state is doubly degenerate. In nonpolar solvents such as benzene, the formation of a tight ion pair may induce an electronic asymmetry in the chromophore, leading to a splitting of the S_1 state. If the anion in the ion pair is located in proximity of the central carbon atom, no effect is expected, but if the anion is located close to one of the three amino groups, as observed in the solid state, a significant splitting of the S_1 state is foreseen.[35]

Because electrostatic forces are decisive for the geometry of the ion pairs, the pronounced splitting of the low-energy absorption band of compound **5a** in benzene strongly supports the previous conclusion that the amino groups carry a substantial part of the positive charge.

Electrochemistry. The electrochemical reduction and oxidation of compound **5a** was studied by cyclic voltammetry in MeCN. Compound **5a** shows two closely spaced one-electron oxidations which at short time scales (scan rates above 100 V s^{-1}) become chemically reversible. The formal potentials for the two oxidations were determined to be 1.30 and 1.37 V vs SCE, respectively. The two consecutive oxidations correspond to the formation of the dication radical and the trication, a behavior resembling the reported two-electron oxidation of crystal violet (CV) at 0.98 V vs SCE.[45]

The reduction of **5a** proved to be chemically irreversible even at a potential scan rate of 5000 V s^{-1}. Thus, direct determination of the formal potential for the reduction process was not possible. Coulometry at constant current in MeCN under strictly anaerobic conditions showed that the reduction was a clean 1 F process. The product obtained upon electrochemical reduction was highly air sensitive and was reoxidized to the starting material, **5a**, on contact with the atmosphere. The reoxidation process was followed by UV−vis spectroscopy, and complete recovery of **5a** was observed. The UV−vis spectrum of the product of the electrochemical reduction showed no absorption in the visible region, and the FABMS spectrum obtained using a matrix containing trifluoroacetic acid (TFA) showed signals corresponding to the mass of a protonated dimer and the mass of a complex between a dimer and TFA, along with strong signals corresponding to **5a**. In accord with these results, we propose that the radical formed by reduction of **5a** dimerizes in a fast process leading to the symmetrical center-to-center dimer.[46−48]

Assuming that the dimerization is a simple second-order reaction between two radicals,[49] a lower limit of the second-order rate constant for dimerization in the order of $k = 10^9$ M^{-1} s^{-1} can be estimated[50] from the absence of any reoxidation current at 5000 V s^{-1} in the cyclic voltammogram of a 1 mM solution of **5a** in MeCN, that is, the rate of the dimerization reaction is close to that of a diffusion-controlled process. On the basis of the same mechanistic assumption, a value of $k = 10^9$ M^{-1} s^{-1} allows an estimate of the formal potential of the reduction process to be −1.1 V vs SCE from the peak potential measured at 1 V s^{-1} (see the Experimental Section).

The very fast reaction of the radical formed by reduction of **5a** may be attributed to the planarity of **5a** and the corresponding radical which leaves the central carbon atom unshielded, in contrast to the central carbon atoms in CV and other nonbridged triarylcarbenium ions, which are shielded by the *ortho* hydrogens. An increase of the rate of reaction with water by a factor of 10^4 is observed when comparing the unshielded TOTA cation with CV.[51]

Conclusions

We have presented a straightforward synthetic procedure leading to a novel class of highly stabilized carbenium ions **5**. The synthetic route is the first example of a selective, stepwise introduction of amino substituents in the *para* positions of triarylcarbenium ions, using the S_NAr reaction. This strategy may be used in the synthesis of a wide variety of complex carbenium ions such as **2**, **3**, **4**, and **5**. It also opens an alternative route to *12c*-methylated derivatives of compound **5** (e.g., **6a**).

The thermodynamic stability of the tris(diethylamino)trioxatriangulenium ion (**5a**) has been evaluated in terms of the pK_{R+} value, using a new acidity function $C\_$ developed for the present purpose. A pK_{R+} value of 19.7 has been measured for **5a**, which is 10 orders of magnitude higher than the values for the most stable carbenium ions previously reported.[3,4] This exceptional stability of the cation **5a** is attributed to the favorable conditions for charge delocalization to the amino groups provided by the planar TOTA system. The pronounced delocalization of the positive charge is reflected in the X-ray structure of the cation **5b** and in the solvatochromy of **5a**, indicating that the effect is present in the solid state as well as in solution. The features of the tris(dialkylamino)trioxatriangulenium ions can be rationalized if one regards the system as a hybrid between TOTA and CV.

Experimental Section

Synthetic Methods and Materials. All reagents used were standard grade unless otherwise mentioned. Ether and THF were dried by

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distillation from Na/benzophenone under nitrogen. Benzene was dried by standing over Na. DMF was purified by distillation from CaH_2 under vacuum. NMR spectra were recorded on a 250 or 400 MHz spectrometer. FABMS spectra were obtained using 1,4-dicyanobutane as matrix. UV−vis spectra were obtained with a Perkin-Elmer Lambda 16 spectrophotometer. Melting points were determined by DSC on a Perkin-Elmer DSC-4.

Elemental analysis was done at the University of Copenhagen, Department of Chemistry, Elemental Analysis Laboratory, Universitetsparken 5, 2100 Copenhagen, Denmark. In general, standard analysis of the carbenium salts with fluorinated anions yielded low values in carbon. Acceptable values were obtained in most cases, however, when a combustion catalyst (V_2O_5) was added. Still, for **2a-BF$_4$**, **3a-PF$_6$**, **4a-PF$_6$**, **4b-BF$_4$**, and **4c-PF$_6$**, analysis of the recrystallized compounds showed values in carbon, hydrogen, and nitrogen at only 93−98% of the calculated values. In each case, however, column chromatography (silica, ether/ethanol) on small amounts produced (in almost quantitative yields) samples showing the acceptable analytical values cited below. No other fractions were observed from the column, and the NMR and mass spectra were unaltered by the chromatographic purification. Therefore, it is believed that the discrepancies were due to the presence of small amounts of inorganic salts such as KPF_6 in the prechromatographed samples. Consequently, these were used without further purification in the subsequent synthetic steps.

Tris(2,4,6-trimethoxyphenyl)carbenium Tetrafluoroborate (1-BF$_4$). A solution of phenyllithium was prepared by addition of bromobenzene (24.5 g, 156 mmol) in dry ether (50 mL) to lithium wire (2.30 g, 328 mmol) in dry ether (100 mL). 1,3,5-Trimethoxybenzene (25.1 g, 149 mmol) in dry benzene (100 mL) was added, and the reaction mixture was stirred at room temperature under argon for 70 h. Diethyl carbonate (5.30 g, 45 mmol) in dry benzene (150 mL) was added, and the reaction mixture was refluxed for 3 days. The cooled reaction mixture was poured into NaOH solution (300 mL, 1 M). The phases were separated, and the water phase was extracted with ether. The combined organic phases were dried over $MgSO_4$ and filtered, yielding a clear yellow solution. Addition of aqueous HBF_4 solution (12 mL, 50%, approximately 100 mmol) resulted in immediate precipitation of the deep blue carbenium salt. The dark purple precipitate was filtered off, washed thoroughly with dry ether, and dried over solid KOH to yield 26.0 g (96%) of the crude product. Reprecipation by addition of water to an acetonitrile solution followed by recrystallization from methanol gave the pure compound in 70% overall yield. ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.05 (6H, s), 3.99 (9H, s), 3.59 (18H, s). ^{13}C NMR (400 MHz, $CDCl_3$): δ 169.70, 166.47, 163.93, 118.62, 91.53, 56.52, 56.36. MS (FAB$^+$): *m/z* 513 (M$^+$). UV−vis λ_{max} (nm (log ϵ)) (CH_2Cl_2): 584 (4.55), 467 (3.98), 322 (3.68), 287 (4.02). Anal. Calcd for $C_{28}H_{33}O_9BF_4$: C, 56.01; H, 5.50. Found: C, 55.69; H, 5.64.

Tris(2,4,6-trimethoxyphenyl)carbenium Chloride (1-Cl). This compound was prepared analogously to **1-BF$_4$** (starting with 15.0 g of 1,3,5-trimethoxybenzene). Instead of HBF_4, gaseous HCl was introduced through the hydrolyzed and dried reaction mixture. The dark purple crystalline precipitate was filtered off, washed thoroughly with dry ether, and dried over solid KOH to yield 10.1 g (66%) of the crude product. The MS (FAB$^+$), ^{1}H NMR, and ^{13}C NMR spectra were identical with those of the BF_4 salt.

4-Diethylamino-2,6-dimethoxyphenyl-bis(2,4,6-trimethoxyphenyl)carbenium Tetrafluoroborate (2a-BF$_4$). Crude **1-BF$_4$** (0.55 g, 0.92 mmol) was dissolved in acetonitrile (15 mL), and diethylamine (0.25 g, 3.4 mmol) was added. After 5 min, ether (150 mL) was added and the reaction mixture was cooled on an ice bath. The precipitate was filtered off and washed with ether, yielding 0.55 g (93%). Recrystallization from methanol gave dark red crystals of compound **2a-BF$_4$** in 76% overall yield. ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.07 (4H, s), 5.80 (2H, s), 3.86 (6H, s), 3.75 (4H, q, J = 7.1 Hz), 3.59 (6H, s), 3.57 (12H, s), 1.38 (6H, t, J = 7.1 Hz). ^{13}C NMR (250 MHz, $CDCl_3$): δ 167.38, 163.31, 161.04, 159.89, 155.05, 123.70, 117.03, 91.42, 89.94, 56.82, 56.75, 55.81, 47.39, 13.59. MS (FAB$^+$): *m/z* 554 (M$^+$). Anal. Calcd for $C_{31}H_{40}NO_8BF_4$: C, 58.04; H, 6.24; N, 2.18. Found (after chromatography, see above): C, 57.92; H, 6.33; N, 2.14. UV−vis λ_{max} (nm (log ϵ)) (CH_2Cl_2): 558 (4.44), 428 (3.96) (sh), 350 (3.96).

Bis(4-diethylamino-2,6-dimethoxyphenyl)-2,4,6-trimethoxyphenylcarbenium Hexafluorophosphate (3a-PF$_6$). Crude **1-BF$_4$** (2.0 g, 3.3 mmol) was dissolved in acetonitrile (20 mL), and diethylamine (15 mL, 144 mmol) was added. After 20 h at room temperature, the excess diethylamine and solvent were removed in vacuo. The dark blue solid was dissolved in ethanol (30 mL), and aqueous KPF_6 solution (100 mL, 0.2 M) was added. The precipitate was filtered off, washed thoroughly with water, and dried over solid KOH. Recrystallization from ethanol gave 1.90 g (78%) of dark blue crystals of the PF_6 salt. ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.09 (2H, s), 5.73 (4H, s), 3.87 (3H, s), 3.6−3.5 (26H, m), 1.30 (12H, t, J = 7.1 Hz). ^{13}C NMR (250 MHz, $CDCl_3$): δ 164.62, 163.23, 160.35, 156.15, 155.05, 117.62, 117.39, 91.74, 88.94, 56.86, 56.42, 55.84, 45.96, 13.33. MS (FAB$^+$): *m/z* 595 (M$^+$). Anal. Calcd for $C_{34}H_{47}N_2O_7PF_6$: C, 55.13; H, 6.35; N, 3.78. Found (after chromatography, see above): C, 54.86; H, 6.43; N, 3.76. UV−vis λ_{max} (nm (log ϵ)) (CH_2Cl_2): 650 (4.72), 550 (4.14) (sh), 425 (3.84), 380 (3.81).

Tris(4-diethylamino-2,6-dimethoxyphenyl)carbenium Hexafluorophosphate (4a-PF$_6$). Compound **1-BF$_4$** (4.0 g, 6.7 mmol) was dissolved in NMP (40 mL), and diethylamine (80 mL, 770 mmol) was added. After 9 days at room temperature, the reaction mixture was poured into aqueous KPF_6 solution (300 mL, 0.2 M). The blue precipitate was washed thoroughly with water and dried over solid KOH. Recrystallization from ethanol gave 3.72 g (71%) of blue needles. ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.70 (6H, s), 3.50 (18H, s), 3.46 (12H, q, J = 7.1 Hz), 1.23 (18H, t, J = 7.1 Hz). ^{13}C NMR (400 MHz, $CDCl_3$): δ 163.20, 154.12, 153.83, 115.03, 88.52, 55.89, 45.05, 12.78. MS (FAB$^+$): *m/z* 636 (M$^+$). Anal. Calcd for $C_{37}H_{54}N_3O_6PF_6$: C, 56.73; H, 6.71; N, 5.34. Found (after chromatography, see above): C, 56.84; H, 6.96; N, 5.37. UV−vis λ_{max} (nm (log ϵ)) (CH_2Cl_2): 643 (4.95), 340 (4.26) (sh), 310 (4.68), 262 (4.54).

Tris(4-diethylamino-2,6-dimethoxyphenyl)carbenium Chloride (4a-Cl). Diethylamine (16 g, 220 mmol) was added to a solution of crude **1-Cl** (1.0 g, 1.8 mmol) dissolved in dry DMF (10 mL). After 4 days at room temperature, the excess diethylamine was removed in vacuo. The remaining dark blue solution was adsorbed on silica (12 g) and washed thoroughly with ether. Purification by column chromatography on silica with ether/ethanol as eluent yielded 0.81 g (66%) of compound **4a-Cl**. The MS (FAB$^+$), ^{1}H NMR, and ^{13}C NMR spectra were identical with those of the PF_6 salt. Anal. Calcd for $C_{37}H_{54}N_3O_6Cl$: C, 66.10; H, 8.10; N, 6.25. Found: C, 66.06; H, 8.14; N, 6.22.

Tris(4-pyrrolidinyl-2,6-dimethoxyphenyl)carbenium Tetrafluoroborate (4b-BF$_4$). Crude **1-BF$_4$** (2.0 g, 3.3 mmol) was dissolved in acetonitrile (30 mL), and pyrrolidine (5 mL, 56 mmol) was added over a period of 10 min. After 20 h at room temperature, the excess amine and solvent were removed in vacuo. Recrystallization from ethanol gave 1.83 g (77%) of blue needles. ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.63 (6H, s), 3.55 (18H, s), 3.49 (12H, t, J = 6.4 Hz), 2.10 (12H, s, J = 6.4 Hz). ^{13}C NMR (250 MHz, $CDCl_3$): δ 163.50, 155.00, 153.75, 115.68, 89.42, 48.57, 25.67. MS (FAB$^+$): *m/z* 630 (M$^+$). Anal. Calcd for $C_{37}H_{48}N_3O_6BF_4$: C, 61.96; H, 6.74; N, 5.86. Found (after chromatography, see above): C, 61.61; H, 6.85; N, 5.77.

4-Diethylamino-2,6-dimethoxyphenyl-bis(4-morpholinyl-2,6-trimethoxyphenyl)carbenium Tetrafluoroborate (4c-BF$_4$). Compound **2a-BF$_4$** (0.27 g, 0.42 mmol) was dissolved in dry DMF (7 mL), and morpholine (7 mL, 80 mmol) was added. After 20 h at room temperature, the reaction mixture was adsorbed on silica and washed thoroughly with ether and dichloromethane before the blue compound was washed out with dichloromethane/ethanol. The solvent was removed in vacuo, and the blue solid was recrystallized from dichloromethane by addition of ether to yield 270 mg (85%) of blue microcrystals. ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.94 (4H, s), 5.72 (2H, s), 3.85 (8H, t, J = 4.8 Hz), 3.62 (4H, q, J = 7.2), 3.54 and 3.53 (18H, two overlapping singlets), 3.31 (8H, t, J = 4.8 Hz), 1.30 (6H, t, J = 7.1). ^{13}C NMR (400 MHz, $CDCl_3$): δ 165.63, 160.98, 157.89, 154.96, 154.81, 119.53, 116.30, 91.08, 88.73, 66.43, 56.22, 56.12, 47.82, 46.03, 12.94. MS (FAB$^+$): *m/z* 664 (M$^+$). Anal. Calcd for $C_{37}H_{50}N_3O_8BF_4$: C, 59.13; H, 6.71; N, 5.59. Found (after chromatography, see above): C, 58.89; H, 6.84; N, 5.54.

Ring Closure. All the ring-closure reactions were performed by heating the corresponding hexamethoxy compounds with 10 equiv of anhydrous LiI in NMP (40−50 mL/g LiI) to 170 °C for 4 h. The synthesis of 2,6,10-tris(diethylamino)-4,8,12-trioxatriangulenium hexafluorophosphate (**5a-PF$_6$**) is given as a representative example.

2,6,10-Tris(diethylamino)-4,8,12-trioxatriangulenium Hexafluorophosphate (5a-PF$_6$). Compound **4a-Cl** (0.50 g, 0.74 mmol) and LiI (1.0 g, 7.5 mmol) were dissolved in NMP (50 mL) and heated to 170 °C for 4 h under nitrogen. The reaction mixture was allowed to cool and was poured into 250 mL of aqueous KPF_6 solution (0.2 M). The precipitate was dissolved in dichloromethane, and the solution was washed thoroughly with aqueous KPF_6 solution (0.2 M). The solvent was removed in vacuo, and the residue was reprecipitated twice by addition of ether to a dichloromethane solution, yielding 0.4 g of a light brown solid. This was purified on a short column of silica with dichloromethane/ethyl acetate (2:1) as eluent. Recrystallization from methanol gave 250 mg (52%) of orange needles. ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.35 (6H, s), 3.51 (12H, q, $J = 7.1$ Hz), 1.25 (18H, t, $J = 7.1$ Hz). ^{13}C NMR (400 MHz, $CDCl_3$): δ 156.92, 154.89, 131.57, 95.11, 94.99, 46.66, 12.78. MS (FAB$^+$): *m/z* 498 (M$^+$). UV−vis λ_{max} (nm (log ϵ)) (CH_2Cl_2): 471 (5.12), 447 (4.84) (sh), 311 (4.41), 302 (4.30) (sh). Anal. Calcd for $C_{31}H_{36}N_3O_3PF_6$: C, 57.85; H, 5.64; N, 6.53. Found: C, 57.76; H, 5.61; N, 6.49.

2,6,10-Tris(diethylamino)-4,8,12-trioxatriangulenium Tetrafluoroborate (5a-BF$_4$). This compound was synthesized in the same way as the PF_6 salt by using a KBF_4 solution in the workup procedure. Recrystallization was performed from dichloromethane/ethyl acetate yielding 180 mg (41%) of red-orange needles. The MS (FAB$^+$), ^{1}H NMR, ^{13}C NMR, and UV−vis spectra were identical with those of the PF_6 salt. Anal. Calcd for $C_{31}H_{36}N_3O_6BF_4$: C, 63.60; H, 6.20; N, 7.18. Found: C, 63.36; H, 6.28; N, 7.15.

2,6,10-Tris(*N*-pyrrolidinyl)-4,8,12-trioxatriangulenium Hexafluorophosphate (5b-PF$_6$). The LiI-catalyzed ring closure was performed using **4b-BF$_4$** (300 mg, 0.42 mmol). The workup was performed analogously to the synthesis of compound **5a**. Instead of column chromatography, a dichloromethane solution of the crude product was flashed through 1 cm of silica which afterward was washed thoroughly with dichloromethane/ether. After evaporation of the solvent, recrystallization from dichloromethane gave 110 mg (41%) of red-orange needles. In its pure form, the compound showed low solubility at room temperature in common NMR solvents, and no ^{13}C NMR spectra were obtained. ^{1}H NMR (250 MHz, pyridine-d_6): δ 6.41 (6H, s), 3.22 (12H, t, br), 1.73 (12H, t, br). MS (FAB$^+$): *m/z* 492 (M$^+$). UV−vis λ_{max} (nm (log ϵ)) (CH_2Cl_2): 473 (5.13), 447 (4.83) (sh), 311 (4.43), 302 (4.32) (sh). Anal. Calcd for $C_{31}H_{30}N_3O_3PF_6$: C, 58.40; H, 4.74; N, 6.59. Found: C, 58.06; H, 4.77; N, 6.44.

2-(Diethylamino)-6,10-bis(*N*-morpholinyl)-4,8,12-trioxatriangulenium Hexafluorophosphate (5c-PF$_6$). The LiI-catalyzed ring closure was performed using **4c-BF$_4$** (200 mg, 0.27 mmol). The workup was performed analogously to the procedure used for compound **5b**, except for using dichloromethane/THF as eluent. Recrystallization from dichloromethane/ethyl acetate yielded 40 mg (22%). In its pure form, the compound showed low solubility at room temperature in common NMR solvents, and no ^{13}C NMR spectra were obtained. ^{1}H NMR (250 MHz, pyridine-d_6): δ 6.86 (4H, d, $J = 1.7$ Hz), 6.55 (2H, s), 3.62 (8H, t, $J = 5.0$ Hz), 3.56 (8H, t, $J = 5.0$ Hz), 3.26 (4H, q, $J = 7.0$ Hz), 0.96 (6H, t, $J = 7.0$ Hz). MS (FAB$^+$): *m/z* 526 (M$^+$). UV−vis λ_{max} (nm (log ϵ)) (CH_2Cl_2): 482 (4.95), 462 (4.85) (sh), 450 (4.83) (sh), 351 (3.3), 307 (4.21). Anal. Calcd for $C_{31}H_{32}N_3O_5PF_6$: C, 55.44; H, 4.80; N, 6.26. Found: C, 55.48; H, 4.67; N, 6.21.

2,6,10-Tris(diethylamino)-*12c*-methyl-4,8,12-trioxatriangulene (6a). Methyllithium (5 mL, 1.5 M in ether, 7.5 mmol) was added to a suspension of **5a** (0.5 g, 0.78 mmol) in dry THF (80 mL). After 20 h of stirring, the solution was quenched with dilute ammonium chloride (50 mL). Ether (50 mL) was added, and the organic phase was separated, washed with water, and dried over sodium sulfate. The solvent was removed in vacuo, and the white/orange solid was redissolved in ether and flashed through 1 cm of silica, which afterward was washed thoroughly with ether. Removal of the solvent gave a white compound which upon recrystallization from acetonitrile yielded 0.32 g (80%) of white/colorless crystals. Melting point (DSC) 20 °C/min: 218−228 °C dec. ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.26 (6H, s), 6.36 (12H, q, $J = 7.0$ Hz), 1.45 (3H, s), 1.20 (18H, t, $J = 7.0$ Hz). ^{13}C NMR (250 MHz, $CDCl_3$): δ 154.00, 148.52, 104.70, 45.21, 32.23, 22.71, 12.99. MS (FAB$^+$): 514 *m/z* (M + 1). Anal. Calcd for $C_{32}H_{39}N_3O_3$: C, 74.82; H,7.60; N, 8.18. Found: C, 74.77; H, 7.60; N, 8.26.

Table 1. Crystallographic Data for 2,6,10-Tris(*N*-pyrrolidinyl)-4,8,12-trioxatriangulenium Hexafluorophosphate

compound	**5b-PF$_6$**
formula	$C_{31}H_{30}O_3N_3PF_6$
formula wt	637.55
crystal system	monoclinic
space group	*P*2(1)/*n*
Z	4
a, Å	14.546(3)
b, Å	8.343(2)
c, Å	22.604(5)
α, deg	90
β, deg	95.74(3)
γ, deg	90
V, Å^3	2729.4(9)
ρ, g cm^3	1.552
crystal dimensions, mm	0.15 × 0.025 × 0.020
type of radiation	Mo Kα
μ, mm^{-1}	0.183
T, K	120(2)
number of reflections	27 660
unique reflections (with $I > 2\sigma$)	2148
R_{int}	0.2444
R(F), R_w(F^2) all data	0.0881, 0.2431

2,6,10-Tris(diethylamino)-4,8,12-trioxatriangulene-*12c*-ol (7a). A small amount of KOH powder and DMSO-d_6 (0.5 mL) was placed in an NMR tube, and argon was introduced for 30 min before **5a-PF$_6$** (approximately 5 mg) was added. After a further 10 min of argon purging, the tube was sealed and the spectra of the now colorless solution were recorded. ^{1}H NMR (250 MHz, KOH/DMSO-d_6): δ 6.23 (6H, s), 3.55 (12H, q, $J =$ Hz), 1.11 (18H, t, $J =$ Hz). ^{13}C NMR (250 MHz, KOH/DMSO-d_6): δ 154.16, 148.90, 103.04, 94.87, 48.02, 45.01, 13.18.

X-ray Crystallography. Crystals of compound **5b-PF$_6$** were mounted on a glass capillary using epoxy glue. Data were collected on a Siemens SMART platform diffractometer with a CCD area sensitive detector. Absorption corrections were made using SADABS.[52] Direct methods for the structure solution and full-matrix least-squares refinements were used. Hydrogen atoms were included in calculated positions. Programs used were SMART, SAINT, and SHELXTL from Siemens.[53,54] The structure was checked for overlooked symmetry using MISSYM and for voids in PLATON.[55] Crystallographic data are given in Table 1. Atomic coordinates and further crystallographic details have been deposited with the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

Determination of pK_{R+} Values. Stock solutions of **5a** and the 9-(4-dimethylaminophenyl)-3,6-di(dimethylamino)xantenium ion (OCV) in DMSO were made from the PF_6 salts. OCV was synthesized by the method described in ref 56. DMSO was purified by distillation from CaH_2 at 10 mmHg argon pressure. Dissolved oxygen was removed from all stock solutions by purging with argon.

The pK_{R+} values of **5a** and OCV were obtained from the relative concentrations of the carbenium ions and the corresponding carbinols, which were determined spectrophotometrically at wavelengths where only the cationic compounds absorb. The total concentration of

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(52) Empirical absorption program (SADABS) written by George Sheldrick for the Siemens SMART platform.

(53) Sheldrick, G. M. *SHELXTL95*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1995.

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carbenium ion and carbinol was constant in all the measurements. The equilibrium distribution K is defined in Equation 3.

$$K = \frac{[\mathrm{ROH}]}{[\mathrm{R}^+]} = \frac{A_0 - A}{A} \qquad (3)$$

A_0 is the absorbance of the pure cation at the wavelength chosen, and A is the absorbance at the same wavelength in the current solution. In all the solvent mixtures used, the solvatochromic effects on the absorption spectra of the carbenium ions were investigated and found to be negligible in relation to the p$K_{\mathrm{R}+}$ measurements. The p$K_{\mathrm{R}+}$ values were derived from linear fits to plots of log K vs pH (in water) and $C\_$ in the DMSO/water/Bu_4NOH system. The $H\_$ values of the individual solutions were determined from linear fits to the data given in ref 30 for the given range of concentrations, that is, 10−20 mol % DMSO for OCV and 40−70 mol % DMSO for **5a**.

The p$K_{\mathrm{R}+}$ value of OCV was determined from the absorbance at 545 nm in a series of aqueous KCl/NaOH buffer solutions. A_0 was determined as the absorbance of OCV at 545 nm in 0.20 M KCl solution with pH adjusted to 8. The p$K_{\mathrm{R}+}$ value of OCV was found to be 13.51. The slope of the linear log K/pH plot was 0.98.

All the equilibrium measurements in the DMSO/water/Bu_4NOH system were performed with solutions containing 0.011 M Bu_4NOH. The molar fraction of DMSO in the individual solutions was calculated by weighing the amount of water, Bu_4NOH stock solution (in water), DMSO, and stock solution of the carbenium salts in pure DMSO. The accuracy of the method applied relative to the predefined $H\_$ function was tested by the determination of the pK_a value of 4-chloro-2-nitroaniline which was found to be 17.12, with a slope of 0.99 for the linear log $K/H\_$ plot. Dolman et al. report pK_a = 17.08 for this compound.[30]

The equilibrium distribution of **5a**/**7a** in the DMSO/water/Bu_4NOH system was determined in seven solutions containing from 43 to 70 mol % DMSO. The linear fit to log K vs $H\_$ had a slope of 1.31 and $K = 1$ at 56.5 mol % DMSO ($H\_ = 18.1$). A_0 was determined as the absorbance of **5a** at 480 nm in 50 mol % DMSO/water solution without Bu_4NOH.

The equilibrium distribution of OCV and its carbinol in the DMSO/water/Bu_4NOH system was determined in five solutions containing from 10 to 20 mol % DMSO. The linear fit to log K vs $H\_$ had a slope of 1.30 and $K = 1$ at 12.1 mol % DMSO ($H\_ = 13.42$). A_0 was determined as the absorbance of OCV at 548 nm in 10 mol % DMSO/water solution without Bu_4NOH.

The new acidity function $C\_$, which was used for the determination of the p$K_{\mathrm{R}+}$ value of **5a**, was constructed by modifying Dolman and Stewart's $H\_$ function.[30] To represent the $H\_$ function by a continuous mathematical function, a third-order polynomium was fitted to the mol % DMSO/$H\_$ data from ref 30 in the whole range from 10 to 70 mol % DMSO (eq 4). The $C\_$ function was obtained by multiplying the coefficients in eq 4 by 1.31 (eq 5) and giving the constant term k' a value so the new function $C\_$ returns the right p$K_{\mathrm{R}+}$ = 13.51 for OCV, which was determined in water (eq 6).

$$H_- \approx aX + bX^2 + cX^3 + k \qquad (4)$$

$$C_- = 1.31(aX + bX^2 + cX^3) + k' \qquad (5)$$

$$k' = \frac{13.51}{1.31(aX + bx^2 + cX^3)};\ X = 12.1 \qquad (6)$$

The $C\_$ function depends on mol % DMSO (X) as:

$$C\_(X) = 11.572 + 0.1756X - 0.00189X^2 + (1.925 \times 10^{-5})X^3$$

By use of this equation, p$K_{\mathrm{R}+}$ = 19.7 was obtained for **5a**.

Voltammetry of 5a (1 mM) was carried out in MeCN (0.1 M Bu_4NPF_6 or 0.1 M Me_4NBF_4) under nitrogen. Electrodes, cells, and instrumentation were identical to what has been described previously,[57] except that the working electrode was a Pt electrode, $d = 0.6$ mm.

Ferrocene/ferrocenium was used as an external potential reference ($E^{\circ\prime}(\mathrm{Fc/Fc^+}) = 0.440$ V vs SCE). The values of $E^{\circ\prime}$ for the two consecutive oxidations of **5a** were determined as the midpoint potentials, $E^{\circ\prime}(1) = E_p(\mathrm{ox1}) - E_p(\mathrm{red1})$ and $E^{\circ\prime}(2) = E_p(\mathrm{ox2}) - E_p(\mathrm{red2})$, measured at a scan rate equal to 100 V s^{-1}. The estimate of the formal potential for the reduction of **5a** was based on application of eq 7,

$$E_p - E^{\circ\prime} = \frac{RT}{n\mathrm{F}}\left[-0.902 + \frac{1}{3}\ln\left(\frac{4}{3}\frac{kC^\circ RT}{n\mathrm{F}\nu}\right)\right] \qquad (7)$$

which is valid for a simple irreversible dimerization of the primary electrogenerated intermediate,[58] from the reduction peak potential measured at $\nu = 1$ V s^{-1} at $C^\circ = 10^{-3}$ M and an estimated value of the second-order rate constant, k, equal to 10^9 M^{-1} s^{-1}.

Coulometry was carried out in a divided cell containing approximately 30 mL catholyte, MeCN (0.1 M Me_4NBF_4), and 8.2×10^{-5} mol **5a**, using a platinum mesh cathode. The coulometry was carried out using constant current, $I = 10$ mA, under strictly anaerobic conditions. The concentration of **5a** during coulometry was followed by determination of the height of the voltammetric reduction peak once per minute (after interruption of the reduction and the stirring). The decay in the concentration of **5a** was strictly linear with charge consumption, and linear regression gave $n = 0.97$. By the end of the coulometric experiment (95% conversion) a sample of the catholyte was removed for UV−vis measurements of the reoxidation before the solvent was evaporated under nitrogen and the residue stored in the dark at −17 °C. This crude product was used in the FABMS experiments described above.

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Supporting Information Available: Tables of fractional coordinates, equivalent isotropic and anisotropic thermal parameters, and bond lengths and bond angles for **5b-PF$_6$** (8 pages). See any current masthead page for ordering information and Web access instructions.

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