Pergamon

Tetrahedron Letters, Vol. 36, No. 10, pp. 1585-1588, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4039/95 $9.50+0.00

0040-4039(95)00094-1

Cation Radicals of 1,3,5-Tris(diarylamino)benzenes

Kurt R. Stickley and Silas C. Blackstock*

Department of Chemistry, Vanderbilt University, Nashville, TN 37235

Abstract: Cyclic voltammetry and ESR studies reveal the nature of the cation radicals of some 1,3,5-tris(diarylamino)benzenes. Results show effectively delocalized radical cations with long solution lifetimes in cold media but with much less kinetic stability at ambient temperature than their monomeric triarylaminium cation radical counterparts. Intramolecular ortho coupling, perhaps via disproportionation, is a postulated cation radical decay mode.

Para-substituted triphenylamine (Ar_3N) cation radicals are quite long-lived and have been extensively studied.[1,2] The unsubstituted $Ph_3N^{+\cdot}$ is, however, a short-lived species whose lifetime is limited by intermolecular *para* coupling of the ion.[2] Thus, kinetically stabile $Ar_3N^{+\cdot}$'s require *para* substitution which retards this coupling. Many *p*-substituted $Ar_3N^{+\cdot}$ species give isolably stable salts which find practical use as easy-to-handle chemical oxidants. We felt that, as a relatively stable spin center, the triarylaminium cation group might be well-suited for incorporation into polyfunctional structures designed to promote intramolecular spin alignment.[3] In pursuit of this objective, we have prepared a series of 1,3,5-tris(diarylamino)benzenes (TAB's) **2** and report here their synthesis and one-electron oxidation properties.

A variety of TAB's can be prepared as shown in Scheme 1 according to a route used previously by Ishikawa and co-workers.[4] Condensation of phloroglucinol dihydrate with substituted anilines (1:4.5 molar ratio), as originally reported by Buu-Hoï,[5] gives 1,3,5-tris(arylamino)benzenes **1**. The resultant triamines **1** are then reacted via a triple Ullmann coupling with the appropriate *p*-substituted iodobenzene at 180 °C for 24 h to afford **2** in low to moderate yield. Crude products are generally isolated by precipitation from methanol and are subsequently recrystallized from acetone/ethanol mixtures. Table I gives purified yields (unoptimized) of compounds **1** and **2** whose structures have been confirmed by NMR analysis.[6]

SCHEME 1

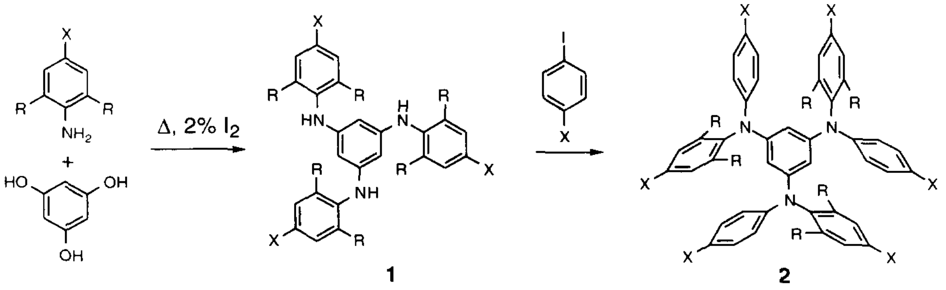


Table I. 1,3,5-Tris aryl (& diaryl) aminobenzenes.

X	R	TAB	
H	H	(**1a**)[5] 18%	(**2a**)[4,7] 45%
CH_3	H	(**1b**) 52%	(**2b**)[8] 44%
t-Bu	H	(**1c**) 14 %	(**2c**) 20%
OBn	H	(**1d**) 29%	(**2d**) 2%
OCH_3	H	(**1e**)[5] 60%	(**2e**)[9] 45%
CH_3	CH_3	(**1f**) 14%	(**2f**) 0.3%

Oxidation of the TAB derivatives by cyclic voltammetry (CV) allows determination of their formal oxidation potential, $E^{\circ\prime}$, for single electron loss (Table II).[10] As the *p*-substituent becomes more electron donating, $E^{\circ\prime}$ for the substrate decreases. Also shown in Table II are the $E^{\circ\prime}$ values for the corresponding Ar_3N species. While these sets of data derive from different solvent conditions,[11] it is nevertheless striking how closely the TAB derivatives parallel the monoamines in $E^{\circ\prime}$. Thus, there appears to be little effect of one meta N atom on another in the TAB's as judged by ease of oxidation for initial electron loss. This is consistent with the cross-conjugative nature of the amino group connection to the phenyl core which prohibits direct overlap of the nitrogen lone pairs. The effect of multiple Ar_2N groups in the TAB structures **2** shows up in the ease of removal of a second electron from the system as compared to two-electron oxidation of Ar_3N. For example, the anodic peak potential for dication formation, $E_{pa}(2)$, for **2b** is 1.13 and for tri-*p*-tolylamine is 1.54,[12] consistent with the presence of three rather independent redox centers in the former and only one in the latter. For **2e**, $\Delta E^{\circ\prime}(1,2)$ is only 0.23 V and $\Delta E^{\circ\prime}(2,3)$ only 0.16 V. We conclude that the primary *thermodynamic* effect of having three meta-linked Ar_2N groups on a phenyl core, as opposed to a single Ar_2N group, is to facilitate the ease of dication and trication formation, with little effect on radical cation formation.

Table II. Formal oxidation potentials ($E^{\circ\prime}$) for some TAB's and Ar_3N's (V vs. SCE).

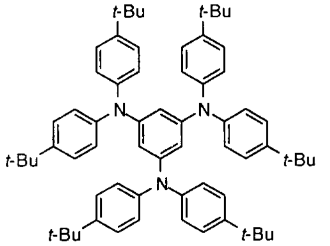
TAB Substrate[a]	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**
$E^{\circ\prime}(1)$[b]	0.95	0.82	0.81	0.69	0.65	0.81
$E^{\circ\prime}(2)$					0.88	
Ar_3N Substrates[c]						
$E^{\circ\prime}(1)$	0.92[2]	0.75[2]	0.76[12]		0.52[2]	

a) CH_2Cl_2 (0.1 M Bu_4NBF_4) b) $E^{\circ\prime}$ for **2a**[7] and **2b**[8] have been previously measured as 1.00 and 0.74, respectively c) CH_3CN (0.1 M Et_4NClO_4)

Only in the case of the *p*-OMe substituted system, **2e**, is enough kinetic stability imparted to 2^{++} to yield a long-lived dication intermediate on the CV timescale (msec). At -78 °C, the third oxidation wave for **2e** becomes electrochemically reversible,[3] but still the dications and trications of the other substrates of Table II remain short-lived. The < msec lifetimes of especially $\mathbf{2b}^{++}$ and $\mathbf{2c}^{++}$ surprised us. To the extent these dications might be viewed as dual, weakly interacting intramolecular $Ar_3N^{+\cdot}$ moieties, we had expected their lifetimes would be comparable to the corresponding $Ar_3N^{+\cdot}$ molecules, but such is not the case. In fact, even the monocations $\mathbf{2b}^{+\cdot}$ and $\mathbf{2c}^{+\cdot}$ decay in seconds to minutes in solution at room temperature, although they are stable for hours below -40 °C. We suspect that facile intramolecular coupling at the ortho positions of adjacent aryl rings may be responsible for the short cation lifetimes but have yet to isolate any decomposition products. One possibility is that $\mathbf{2}^{++}$, which is accessible by disproportionation of $\mathbf{2}^{+\cdot}$ (only ~

5 kcal mol^{-1} endothermic for the TAB$^{+\cdot}$'s), undergoes a biradical intramolecular ortho coupling.[13] The greater kinetic stability observed for **2e**$^{++}$ may result from the strong *p*-OMe donors diminishing the ortho spin density in this case.[14] However, it is notable that even the ortho-substituted derivative **2f** does not give a long-lived dication. We are continuing to explore the structure/lifetime relationship for other **2**$^{++}$ derivatives.

ESR spectra of four **2**$^{+\cdot}$'s generated by chemical oxidation of **2** by one molar equiv of thianthrenium perchlorate ($TH^+ClO_4^-$)[15] (CAUTION)[16] in CH_2Cl_2 at -78 °C have been obtained. The spectra of **2e**$^{+\cdot}$, **2c**$^{+\cdot}$ and **2d**$^{+\cdot}$ all display a 10-line pattern with a line separation of ~ 3 Gauss. The signals seem to derive from observed a(3N) and a(3H) (core ring hydrogens) splittings of comparable magnitude. The ESR spectrum of **2c**$^{+\cdot}$ and its simulation[17] are shown in Figure 1. In the case of **2b**$^{+\cdot}$, a single broad peak is observed by ESR. The normal fine structure is lost presumably because the small, unresolved a(18H) splitting from the methyl groups effectively broadens the lines. The **2**$^{+\cdot}$ solutions remain ESR active for hours at < -40 °C.



2c

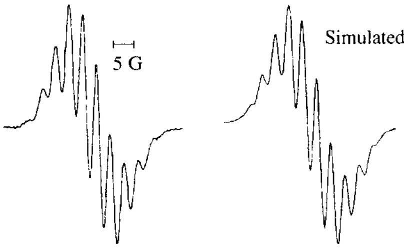
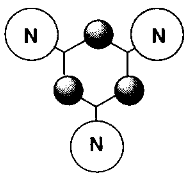
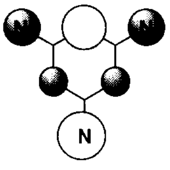


Figure 1. ESR spectrum of **2c**$^{+\cdot}$ at -78 °C in CH_2Cl_2.

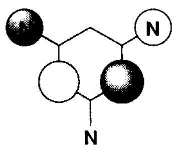
The observed a(3N) splittings suggest that cation radicals of **2** are delocalized structures having three equivalent N atoms or at least that such is the average structure on the ESR timescale. The analogous $Ar_3N^{+\cdot}$ ESR spectra show a(N) values of 9.0 - 9.5 G,[2] and therefore, a(3N) of ~ 3 G appears appropriate for effectively delocalized TAB cation radicals. AM1/UHF calculation[18] of 1,3,5-triaminobenzene cation radical (**3**$^{+\cdot}$) suggests that **3**$^{+\cdot}$ prefers a C_{2v} Jahn-Teller structure (a $^2A_2$ state) in which all NH_2 groups remain conjugated to the phenyl core but the nitrogens exists nominally in two sets. The salient nonbonding (N lone pair rich) MO's are depicted below. For a $^2A_2$ structure to be consistent with the **2**$^{+\cdot}$ ESR data requires



b_1



b_1



a_2

either fortuitous near equivalence of absolute N (2 + 1) and H (2 + 1) spin densities or time averaging of such. It is also possible that the cation radical is actually $^2B_1$, in which real or apparent 3-fold symmetry of the spin density could give the observed ESR spectrum. Distinction between these possibilities, and validation of this semi-empirical prediction, awaits a higher level theoretical analysis. Preparation of an isolably stable cation radical of structure type **2** would allow more in-depth investigation of its structure and is currently one goal of our future work.

Acknowledgment. We thank the National Science Foundation (CHE-9200144) for support of this work and the National Institutes of Health (BRSG), along with Vanderbilt University for support of the chemistry department ESR facility.

References and Notes

1. Hagopian, L.; Günter, K.; Walter, R. I. *J. Phys. Chem.* **1967**, *71*, 2290.
2. Seo, E. T.; Nelson, R. F.; Fritsch, J. M.; Marcoux, L. S.; Leedy, D. W.; Adams, R. N. *J. Am. Chem. Soc.* **1966**, *88*, 3498-3503.
3. Stickley, K. R.; Blackstock, S. C. *J. Am. Chem. Soc.* **1994**, in press.
4. Ishikawa, W.; Inada, H.; Nakano, H.; Shirota, Y. *Mol. Cryst. Liq. Cryst.* **1992**, *211*, 431-438.
5. Buu-Hoï, N. P. *J. Chem. Soc.* **1952**, 4346-4349.
6. NMR's were performed in $CDCl_3$. ^{1}H NMR's were run at 300 MHz and ^{13}C NMR's as indicated. (**1a**) mp 195-196 °C; (lit.[5] 196 °C). (**1b**) mp 189-190 °C; ^{1}H NMR δ 2.38 (s, 9 H), 5.49 (s, 3 H), 6.18 (s, 3 H), 6.94 (d, J = 6 Hz, 6 H), 7.06 (d, J = 6 Hz, 6 H). ^{13}C NMR (50 MHz) δ 20.66, 97.11, 119.54, 129.73, 130.95, 140.05, 146.02. (**1c**) mp 183-184 °C; ^{1}H NMR δ 1.30 (s, 27 H), 5.52 (s, 3 H), 6.23 (s, 3 H), 7.12 (d, J = 8 Hz, 6 H), 7.28 (d, J = 8 Hz, 6 H). ^{13}C NMR (50 MHz) δ 31.44, 34.13, 97.50, 119.00, 125.97, 140.07, 144.23, 145.85. (**1d**) mp 162-164 °C; ^{1}H NMR δ 5.12 (s, 6 H), 5.38 (s, 3 H), 70.37, 94.83, 115.53, 122.31, 127.44, 127.84, 128.49, 135.87, 137.13, 146.97, 154.25. (**1e**) mp 166-167 °C; (lit.[5] 167 °C). (**1f**) mp 188-189 °C; ^{1}H NMR δ 2.14 (s, 18 H), 2.28 (s, 9 H), 4.74 (s, 3 H), 5.09 (s, 3 H), 6.88 (s, 6 H). ^{13}C NMR (75 MHz) δ 18.28, 20.82, 90.28, 128.88, 134.67, 135.63, 136.29, 148.45. (**2a**) mp 256-257 °C (lit.[7] 257-257.5 °C). (**2b**) mp 232-233 °C; ^{1}H NMR δ 2.21 (s, 18 H), 6.28 (s, 3 H), 6.88 (d, J = 6 Hz, 12 H), 6.94 (d, J = 6 Hz, 12 H). ^{13}C NMR (50 MHz) δ 20.70, 112.82, 123.91, 129.49, 131.69, 145.01, 149.01. (**2c**) mp 308-309 °C; ^{1}H NMR δ 1.24 (s, 54 H), 6.42 (s, 3 H), 6.92 (d, J = 8 Hz, 12 H), 7.13 (d, J = 8 Hz, 12 H). ^{13}C NMR (50 MHz) δ 31.42, 34.13, 114.68, 123.01, 125.58, 144.72, 144.82, 148.85. (**2d**) mp 255-256 °C; ^{1}H NMR δ 4.94 (s, 12 H), 6.10 (s, 3 H), 6.74 (d, J = 8 Hz, 12 H), 6.92 (d, J = 8 Hz, 12 H), 7.26-7.40 (m, 30 H). ^{13}C NMR (75 MHz) δ 70.40, 108.93, 115.33, 125.69, 127.49, 127.87, 128.52, 137.12, 141.17, 149.23, 154.53. (**2e**) mp 190-191 °C; (lit.[3] 190-191 °C). (**2f**) mp 239-240 °C; ^{1}H NMR δ 1.84 (s, 18 H), 2.20 (s, 9 H), 2.25 (s, 9 H), 5.98 (s, 3 H), 6.73 (s, 6 H), 6.79 (d, J = 7 Hz, 6 H), 6.90 (d, J = 7 Hz, 6 H). ^{13}C NMR (100 MHz) δ 18.10, 20.53, 20.92, 104.11, 118.68, 128.94, 129.20, 129.34, 135.98, 137.26, 140.07, 143.36, 146.74.
7. Yoshizawa, K.; Chano, A.; Ito, A.; Tanaka, K.; Yamabe, T.; Fujita, H.; Yamauchi, J.; Shiro, M. *J. Am. Chem. Soc.* **1992**, *114*, 5994-5998.
8. Tanaka, H.; Yamaguchi, Y.; Yokoyama, M. *Denshi Shashin Gakkaishi* **1990**, *29*, 366-372.
9. Ogata, M.; Watanuki, T.; Kamisaka, T.; Tsukamoto, K.; Saruwatari, N. *JP Patent 1,219,838* **1989**,
10. Cyclic Voltammograms have been recorded using a three-electrode cell with a planar Pt disc working electrode, a Pt wire counter electrode, and a saturated calomel reference electrode (SCE) separated from the main chamber by a vycor frit.
11. It is our experience that anodic $E^{\circ\prime}$ values in CH_2Cl_2 are typically 0.05 - 0.10 V more positive than in CH_3CN.
12. Reynolds, R.; Line, L. L.; Nelson, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 1087-1092.
13. Ar_3N dications are known to undergo fast intramolecular ortho coupling to give carbazoles (see ref 12 and also Fox, M. A.; Dulay, M. T.; Krosley, K. *J. Am. Chem. Soc.* **1994**, *116*, 10992-10999).
14. While $\mathbf{2d}^{++}$ is also a *p*-alkoxy TAB derivative, we expect that it decomposes by facile O,Bn bond cleavage.
15. Murta, Y.; Shine, H. J. *J. Org. Chem.* **1969**, *34*, 3368-3372.
16. Caution! Thianthrenium perchlorate ($TH^{+}ClO_4^{-}$) is a shock sensitive explosive solid and should be handled in small quantities and with due care.
17. The simulation uses a(3N) 3.55 G, a(3H) 2.55 G, and a linewidth of 1.6 G.
18. Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902-3909.

(*Received in USA* 16 *November* 1994; *revised* 3 *January* 1995; *accepted* 9 *January* 1995)