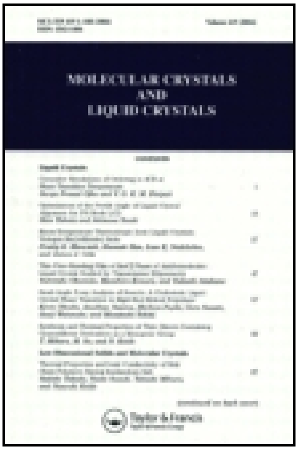

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

# Synthesis of Stable Cationic Radicals of Hindered Hexaamino and Triaminobenzene Derivatives and the Study of their Solid State Magnetic Properties

R. B. Upasani [a] [b] , L. Y. Chiang [c] , D. P. Goshorn [c] & P. Tindall [d]
[a] Corporate Research Laboratory, Exxon Research and Engineering Company, Annandale, New Jersey, 08801
[b] Department of Physics, Princeton University, Princeton, New Jersey, 08544
[c] Corporate Research Laboratory, Exxon Research and Engineering Company, Annandale, New Jersey, 08801
[d] Department of Chemistry, State University of New York, Stony Brook, New York, 11794

To cite this article: R. B. Upasani , L. Y. Chiang , D. P. Goshorn & P. Tindall (1990): Synthesis of Stable Cationic Radicals of Hindered Hexaamino and Triaminobenzene Derivatives and the Study of their Solid State Magnetic Properties, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 190:1, 35-43

To link to this article: http://dx.doi.org/10.1080/00268949008047830

*Mol. Cryst. Liq. Cryst.*, 1990, Vol. 190, pp. 35-43
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Printed in the United States of America

# Synthesis of Stable Cationic Radicals of Hindered Hexaamino and Triaminobenzene Derivatives and the Study of their Solid State Magnetic Properties

R. B. UPASANI

*Corporate Research Laboratory, Exxon Research and Engineering Company, Annandale, New Jersey 08801, Department of Physics, Princeton University, Princeton, New Jersey 08544*

and

L. Y. CHIANG and D. P. GOSHORN

*Corporate Research Laboratory, Exxon Research and Engineering Company, Annandale, New Jersey 08801*

and

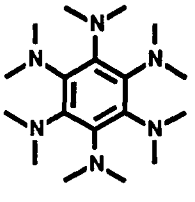
P. TINDALL

*Department of Chemistry, State University of New York, Stony Brook, New York 11794*

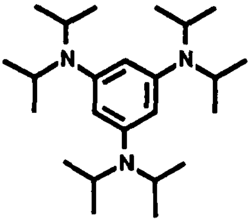
Both hexakis(dimethylamino)benzene (HDMAB) and 1,3,5-tris(diisopropylamino)benzene (TDIAB) were synthesized by improved procedures. In contrast to the irreversibility of electron oxidations of many triaminobenzene derivatives, we demonstrate that, by substituting three hindered diisopropylamino groups on benzene, stable monocationic radicals can be obtained. In the case of HDMAB its cationic radical can be stabilized in a strong acid medium. The observed bulk spin densities of 0.18 – 0.23 spins ½ per donor molecule in TDIAB-$PF_6$ and HDMAB-$PF_6$ solids are significant comparing to the diamagnetic properties normally obtained in solids of simple cationic salts of planar organic donor molecules. The results imply that a small degree of molecular spin separation due to the steric effect can readily increase sharply the paramagnetic spin density of solids.

## INTRODUCTION

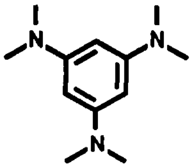
Three dimensional bulk ferromagnetism requires a high density of magnetic spins and a ferromagnetic coupling between spins. Recently, we proposed a synthetic model for ground state bulk ferromagnetism or ferrimagnetism at solid state.[1,2] Experimentally, our approach involves an external doping process to oxidize the organic donors, such as 2,3,6,7,10,11-hexamethoxytriphenylene (HMT) possessing a $D_{3h}$ symmetry, to their dicationic state with triplet spin characters[3] in a pre-arranged solid state structure. A systematic study of this approach has substantiated that the process of vapour phase chemical doping at the solid state of organics can be utilized as a general method for the preparation of high spin density organic solid state materials exhibiting, in some cases, ferromagnetic or ferrimagnetic coupling between spins. Based on a number of experimental results, it seems to be plausible that a mechanism of molecular spin separation induced by dopants at solid state may play a major role in the generation of bulk high density of spins.[4] This observation prompts us to synthesize highly hindered benzene analog organic donors, with a at least $C_3$ symmetry, such as hexakis(dimethylamino)benzene[5] (HDMAB, **1**) and 1,3,5-tris(diisopropylamino)benzene[6] (TDIAB, **2**) to examine the approach of molecular spin separation in solid state. If the spins (either doublet or triplet) in aromatic organics can be sterically separated from each other far enough in solid state to prevent the interspin antiferromagnetic coupling while maintaining a certain degree of spin interaction through space, a material with bulk constructive magnetic properties may be made at low temperatures.



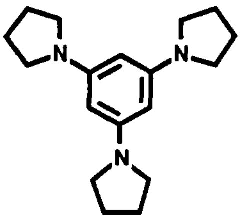
**1 (HDMAB)**



**2 (TDIAB)**



**3**

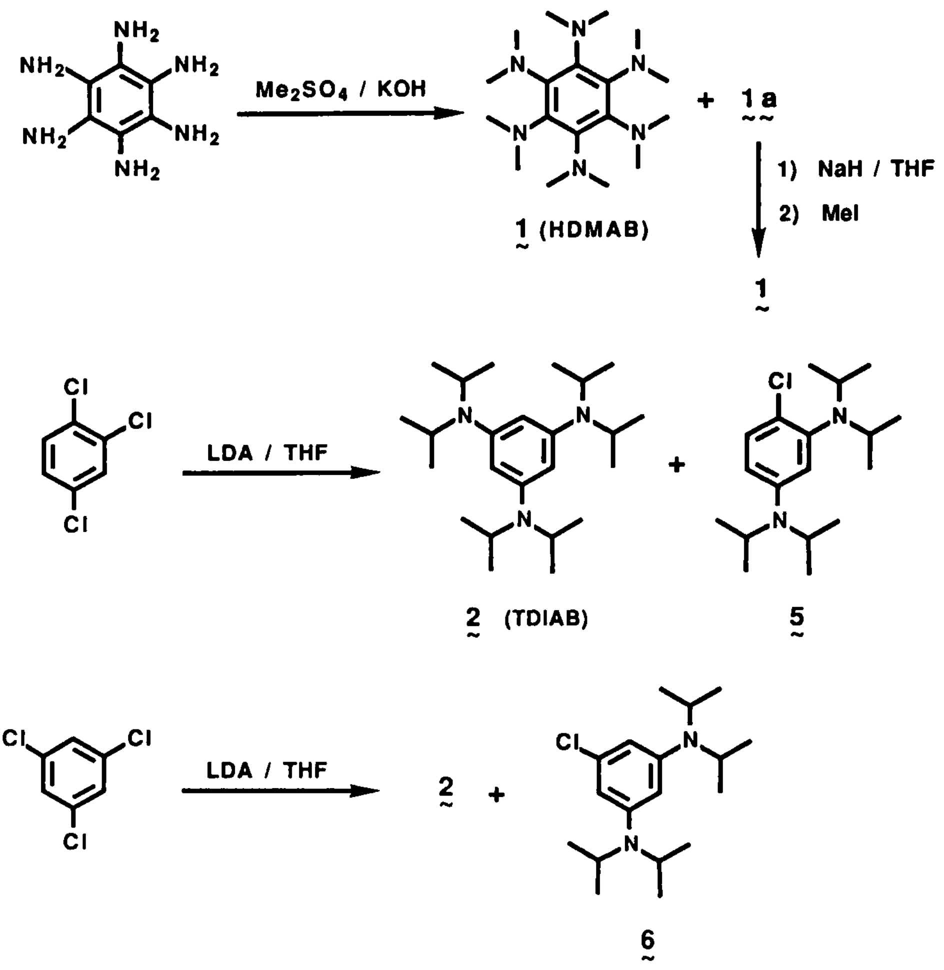


**4**

However, the cationic salts of HDMAB and many triaminobenzene derivatives, such as 1,3,5-tris(dimethylamino)benzene (**3**) and 1,3,5-tris(pyrrolidinamino)benzene (**4**) were found[7] to be unstable showing irreversible electron oxidations in their cyclic voltammetry. Here we report methods to synthesize stable cation radicals of HDMAB and triaminobenzene derivatives and the study of their solid state magnetic properties at different temperatures.

## RESULTS AND DISCUSSION

Both hexakis(dimethylamino)benzene (**1**) and 1,3,5-tris(diisopropylamino)benzene (**2**) can be synthesized by a modified literature procedure.[5,6] We found that permethylation of hexaaminobenzene, which was prepared by the catalytic hydrogenation of 1,3,5-triamino-2,4,6-trinitrobenzene over Pd/C in ethylacetate,[7] with dimethyl sulfate in the presence of base does not give a reported yield[5] of the desirable product HDMAB. It resulted in a mixture of HDMAB (10% yield) and partially methylated products **1a** (52% yield), such as 1,4-bis(methylamino)-2,3,5,6-tetrakis(dimethylamino)benzene and its isomers, as shown in Scheme 1. Compounds



Scheme 1

**1a** can be separated from HDMAB and methylated further by a deprotonation reaction with sodium hydride in THF, followed by a reaction of the resulting intermediate with methyl iodide to afford HDMAB. The irreversibility of electron oxidations of HDMAB at ambient temperature was confirmed by means of the cyclic voltammogram. It shows the first and the second oxidation potential at 0.50 V and 0.93 V *vs.* SCE, respectively. The low stability of cationic HDMAB is mainly due to the high steric hindrance of six dimethylamino groups surrounding benzene that results in a minimum conjugation of $\pi$-electrons with the unpaired electrons of nitrogen. To stabilize the cation radical of this type of molecular system, a proper combination of a suitable degree of steric hindrance around the benzene ring and a maximum conjugation between $\pi$-electrons and unpaired nitrogen electrons is desirable. Indeed, we found that, by substituting all the methyl groups of 1,3,5-tris(dimethylamino)benzene (**3**) by isopropyl groups, a pronounced improvement over the cationic radical stability was observed.

1,3,5-tris(diisopropylamino)benzene (**2**) was prepared in 17% yield from a modified literature procedure[6] using a substitution reaction of 1,2,4-trichlorobenzene with lithium diisopropylamide (LDA) in a mixture of diisopropylamine and tetrahydrofuran as shown in Scheme 1. In this reaction the major product was found to be 1-chloro-2,4-bis(diisopropylamino)benzene (**5**). Alternatively, compound **2** can be synthesized by a similar reaction condition as described above starting from 1,3,5-trichlorobenzene. It gave products as a mixture of TDIAB in 19% yield and 1-chloro-3,5-bis(diisopropylamino)benzene (**6**) in 40% yield.

The cyclic voltammetry of TDIAB as depicted in Figure 1 shows a reversible one-electron oxidation with a half-wave potential of $E_{1/2} = 0.47$ V *vs.* SCE using tetra-*n*-butylammonium hexafluorophosphate as an electrolyte in methylene chloride. The chemical oxidation of TDIAB was carried out by a doping reaction with one equivalent of nitrosonium hexafluorophosphate in acetonitrile under an inert atmosphere to give dark brown solids of TDIAB-$PF_6$ (**7**), which is soluble in many common organic solvents. Interestingly, in the case of HDMAB we found that its monocationic salt can be made by the chemical oxidation of HDMAB in trifluoroacetic acid with one equivalent of nitrosonium hexafluorophosphate in a minimum amount of acetonitrile under an inert atmosphere, followed by the evaporation of solvents to give dark purple solids of HDMAB-$PF_6$ (**8**). During the reaction the trifluoroacetic acid solution of HDMAB turned immediately to purple upon the addition of $NOPF_6$. Without trifluoroacetic acid the same solution turned to purple and then slowly to brown with a decomposition of $HDMAB^{+1}$. The UV-visible spectrum of TDIAB-$PF_6$ and HDMAB-$PF_6$ complexes are shown in Figure 2. It indicates a strong absorption with a peak maximum at 390 nm and a weak absorption at 582 nm for TDIAB-$PF_6$ and a absorption with a peak maximum at 450 nm for HDMAB-$PF_6$.

The formation of monocationic HDMAB radicals was substantiated by the ESR spectroscopic study as shown in the spectrum of Figure 3a, which was taken at

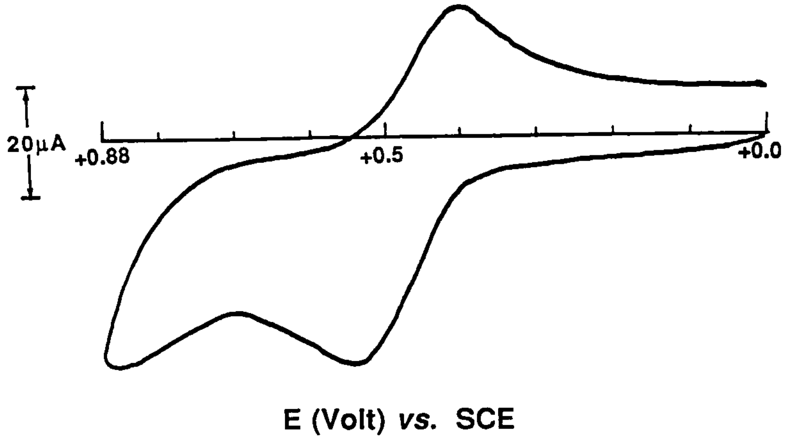


FIGURE 1 The cyclic voltammogram of TDIAB with tetra-*n*-butylammonium hexafluorophosphate as an electrolyte in methylene chloride.

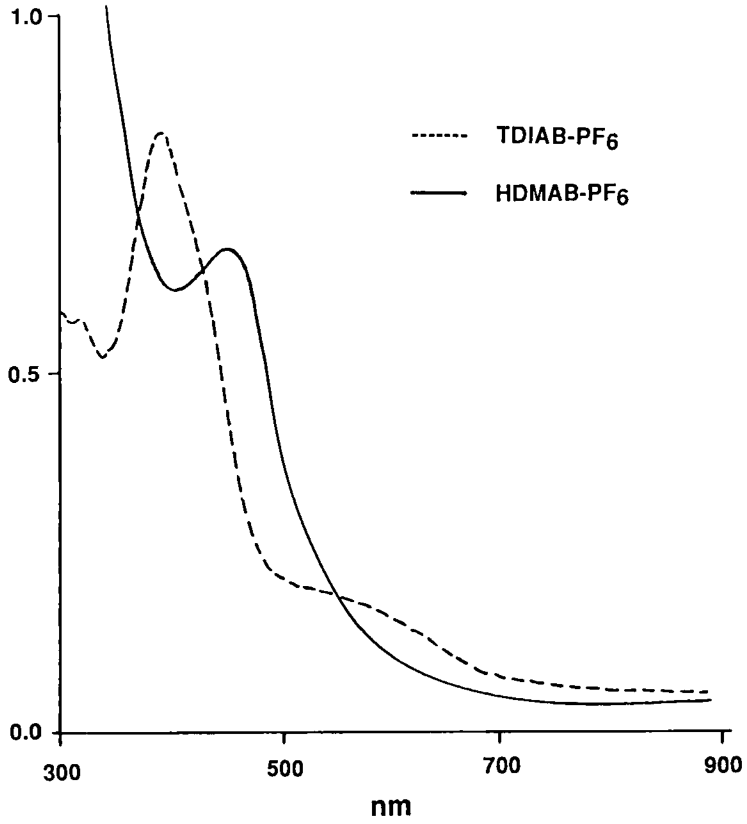


FIGURE 2 The absorption spectrum of TDIAB-PF$_6$ complex in acetonitrile and HDMAB-PF$_6$ complex in a mixture of acetonitrile and trifluoroacetic acid.

130K. A similar spectrum can also be obtained at 300K. The full breadth of the spectrum is approximately 95 G. A hyperfine splitting of 7.3 G was measured from the peak maxima. If this uniformly-spaced splitting persists throughout the breadth, the spectrum would consist of 13 lines, which is consistent with the hyperfine coupling of the unpaired HDMAB radical with six nitrogen atoms ($S = 1$). In the case of the monocationic TDIAB radical, the ESR spectrum (Figure 3b) shows a breadth of approximately 80 G with five broad lines corresponding to the hyperfine coupling of the TDIAB unpaired radical with three nitrogen atoms, where the relative intensities of the sixth and seventh lines being too weak to detect. The hyperfine splitting of these lines was found to be 13.6 G. The nature of this large magnitude of splitting is currently under investigation.

The static magnetic susceptibility ($\chi_g$) data were obtained with a Faraday magnetometer (4K–300K) and a vibrating sample magnetometer (1.3K–4.2K), where the significant contribution of ferromagnetic impurities and the temperature-independent diamagnetic susceptibilities ($\chi_o$) to the measured magnetizations were corrected for *via* magnetization *vs* magnetic field isotherms at several temperatures

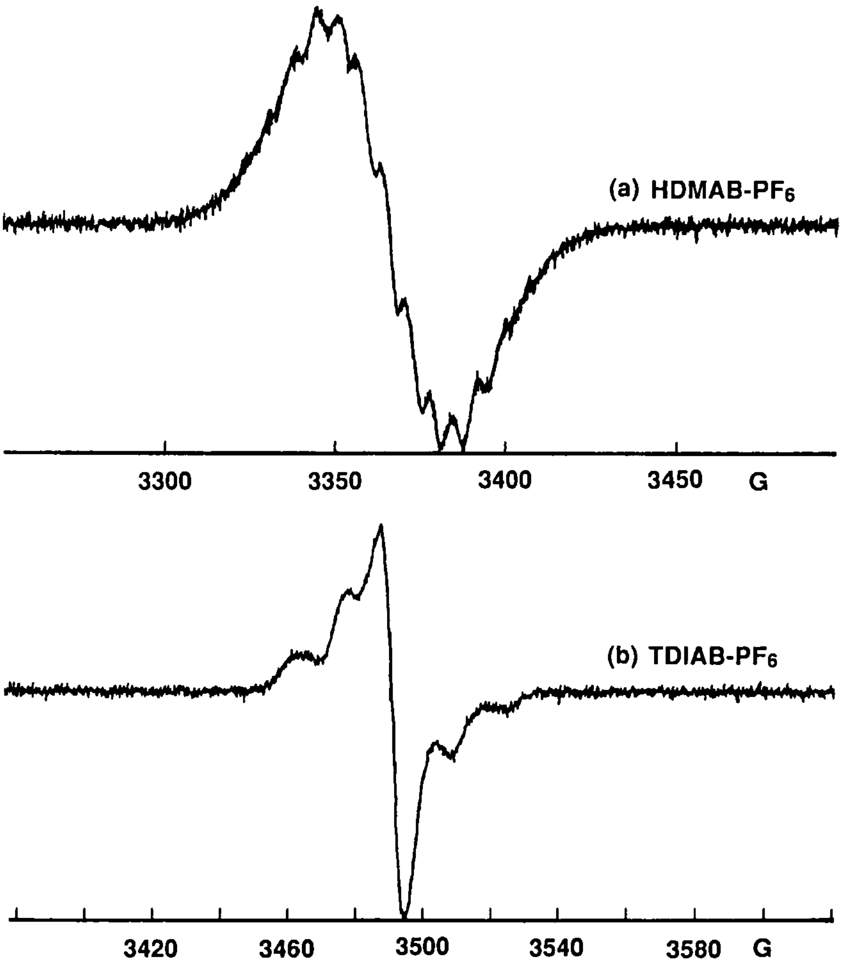


FIGURE 3 The ESR spectrum of (a) monocationic HDMAB solids at 130K showing a hyperfine coupling (13 lines) of radical with six nitrogen atoms and (b) monocationic TDIAB solids at 300K. Both (a) and (b) gives g = 2.003 at the center of spectrum.

for each sample. The spin densities (n) were computed from the molar Curie constant $C_M$ using the relation $C_M = N_{Ag}^2 S(S + 1)m_B^2/3K_B$, where $N_A$ is a Avogadro's number, $m_B$ is the Bohr magneton, $K_B$ is Boltzmann's constant, and where we have assumed the Lande factor g = 2 and spin S = ½. The temperature dependence of reciprocal magnetic susceptibilities $(\chi_g - \chi_o)^{-1}$ of TDIAB-$PF_6$ (**7**) and HDMAB-$PF_6$ (**8**) solids are shown in Figure 4a and 4b, respectively. Both complexes **7** and **8** were found to be paramagnetic with a Curie constant $C_M$ = 0.086 and 0.068 cm³K/mole, corresponding to a spin density of 0.23 spins ½ per TDIAB molecule and 0.18 spins ½ per HDMAB molecule, respectively. The observed large negative Weiss temperature of both complexes reveals that the magnetic interactions between the spins are strongly antiferromagnetic.

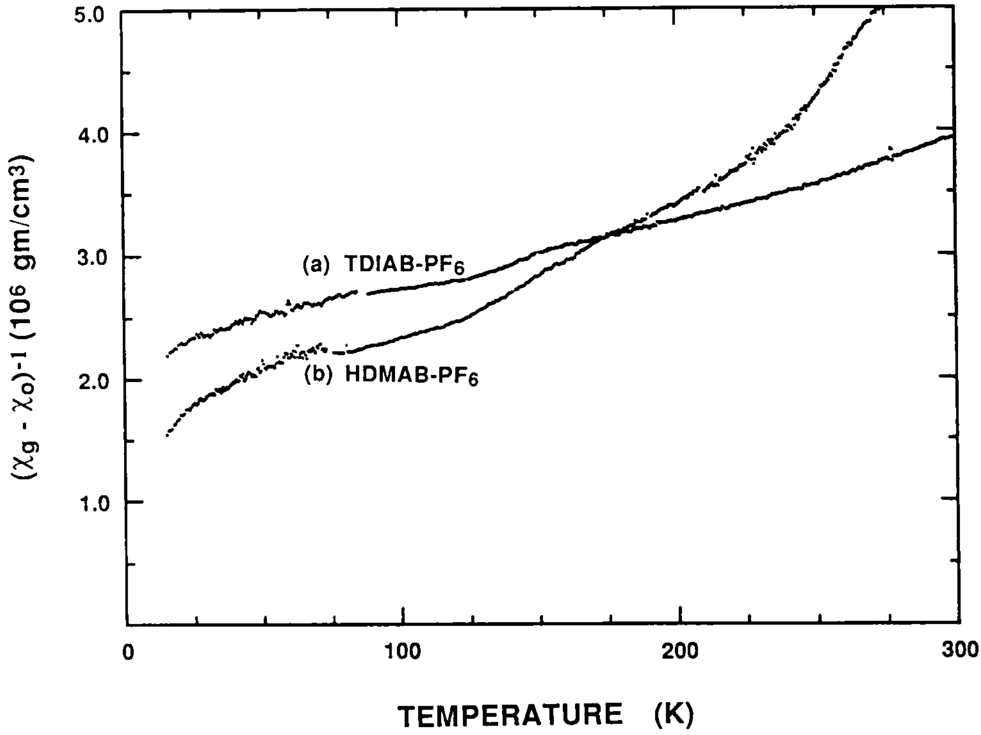


FIGURE 4 The temperature dependence of reciprocal magnetic susceptibilities of (a) TDIAB-$PF_6$ complex and (b) HDMAB-$PF_6$ complex in solid state.

## EXPERIMENTAL

Hexaaminobenzene was prepared from the catalytic hydrogenation reaction of 1,3,5-trinitro-2,4,6-triaminobenzene[7] using Pd/C as a catalyst. Sodium hydride, 1,2,4-trichlorobenzene, 1,3,5-trichlorobenzene, and lithium diisopropylamide in THF were purchased from Aldrich Chemicals and used as received. Tetrahydrofuran was freshly distilled from sodium prior to use.

*Synthesis of Hexakis(dimethylamino)benzene (HDMAB, 1).* A modified Backer's method[5] was used. Hexaaminobenzene (3.5 mmol, 588 mg) was dissolved in aq. KOH (3N, 60 ml) and the solution was treated dropwise with an excess of dimethyl sulfate (20 g) over a period of 30 min. The temperature of the reaction mixture was maintained at 35–40°C. The stirring was continued for an additional 2 hr. The precipitated solid was collected by filtration, washed with water and acetone to remove the by-products **1a**. The dried solid was then recrystallized from acetic acid to afford hexakis(dimethylamino)benzene (**1**, 120 mg) as colorless needles in 10% yield; m.p. 234 – 6°C (lit. 236°C). $^1$H NMR ($CDCl_3$) $\delta$ 2.73 (s, 36H, N-$CH_3$); MS *m/e* 336 ($M^+$, 36), 308 (100), 278 (29), 263 (9), 252 (12), 249 (12) and

235 (12); IR (KBr) $\upsilon_{max}$ 2964, 2910, 2863, 2831, 2769, 1470, 1430, 1392, 1189, 998, and 772 $cm^{-1}$.

From the combined aqueous solution and acetone washings, partially methylated hexaaminobenzenes **1a**, such as 1,4-bis(methylamino)-2,3,5,6-tetrakis(dimethylamino)benzene, were recovered in 52% yield (550 mg); m.p. 165°C. $^1H$ NMR ($CDCl_3$) $\delta$ 2.6–2.9 (m, N-$CH_3$); MS *m/e* 308 ($M^+$). Further methylation of compounds **1a** was carried out as follows. Compounds **1a** (924 mg, 3 mmol) were added slowly to a suspension of sodium hydride (156 mg, 6.5 mmol), which was prepared from NaH in mineral oil and washed with hexane, in THF (30 ml) under an inert atmosphere. After heating at 60°C for 30 min, the mixture was added an excess of methyl iodide (5 ml) and stirred at room temperature for 6 hr. At the end of reaction a small quantity of water was added and the solvent was evaporated. The crude products were extracted by hexane (100 ml), washed with $H_2O$, dried over anhydrous $MgSO_4$, and purified as described above to give hexakis(dimethylamino)benzene (**1**, 500 mg) in nearly 50% yield.

*Synthesis of 1,3,5-tris(diisopropylamino)benzene (TDIAB, **2**).* A modified Effenberger's procedure[6] was used. To a solution of 1,2,4-trichlorobenzene (20 mmol, 3.6 g, 2.65 ml) and diisopropylamine (120 mmol, 12 g, 17 ml) in THF (100 ml, dried over Na) was treated with lithium diisopropylamide (LDA, 105 mmol, 70 ml, 1.5M in hexane) at room temperature. The resulting mixture was stirred at 60°C for 20 hr. The excess of LDA was quenched with aq. $NH_4Cl$. The mixture was extracted with diethyl ether, washed with water, dried over anhydrous $MgSO_4$, and the solvent evaporated to afford a dark oil of crude products (4 g). The crude products were then purified by column chromatography over silica gel using a solvent mixture of hexane-EtOAc (95:5) as an eluent. A band corresponding to $R_f$ = 0.8 was collected to give 1-chloro-2,4-bis(diisopropylamino)benzene (**5**, 2.4 g) in 39% yield as a brown oil; $^1H$ NMR ($CDCl_3$) $\delta$ 1.05 (d, J = 7.5 Hz, 12H, $CH_3$), 1.13 (d, J = 7.5 Hz, 12H, $CH_3$), 3.5 (m, 2H, N-CH), 3.7 (m, 2H, N-CH), 6.7 (dd, J = 2 and 7 Hz, 1H, aromatic), 6.9 (d, J = 2 Hz, 1H, aromatic), and 7.2 (d, J = 7 Hz, 1H, aromatic). The solvent mixture in column was then changed to hexane-EtOAc (90:10). A second band corresponding to $R_f$ = 0.5 was collected to afford 1,3,5-tris(diisopropylamino)benzene (**2**, 1.3 g) in 17% yield as a yellow oil. Product **2** was further purified by distillation under a reduced pressure; $BP_{0.2}$ 112-5°C (lit.[6] $BP_{10^{-4}}$ 98-9°C). $^1H$ NMR ($CDCl_3$) $\delta$ 1.1 (d, J = 7.5 Hz, 36H, $CH_3$), 3.6 (m, 6H, CH), and 6.26 (s, 3H, aromatic); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.8 ($CH_3$), 48.1 (N-CH), 113.0 (H-$C_{aromatic}$), and 147.0 (N-$C_{aromatic}$); IR (KBr) $\upsilon_{max}$ 2964, 2933, 2878, 1586, 1461, 1368, 1189, and 1014 $cm^{-1}$.

Alternatively, 1,3,5-tris(diisopropylamino)benzene can be synthesized by similar reactions condition as described above starting from 1,3,5-trichlorobenzene. It gave products as a mixture of TDIAB in 19% yield and 1-chloro-3,5-bis(diisopropylamino)benzene (**6**) in 40% yield. The analytical data of compound **6**: $^1H$ NMR ($CDCl_3$) $\delta$ 1.2 (d, J = 7.5 Hz, 24H, $CH_3$), 3.75 (m, 4H, CH), and 6.25 (m, 3H, aromatic); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.4 ($CH_3$), 47.7 (N-CH), 108.4 (H-$C_{aromatic}$), 109.3 (H-$C_{aromatic}$), 133.9 (Cl-$C_{aromatic}$), and 149.1 (N-$C_{aromatic}$).

## CONCLUSION

Both hexakis(dimethylamino)benzene (HDMAB) and 1,3,5-tris(diisopropylamino)benzene (TDIAB) were synthesized by improved procedures. In contrast to the irreversibility of electron oxidations of many triaminobenzene derivatives, we found that, by substituting three hindered diisopropylamino groups on benzene, stable monocationic TDIAB radicals can be obtained. The stabilization attributes to a proper degree of steric hindrance around the benzene ring without much interruption of the π and p orbitals interaction. In the case of HDMAB its cationic radicals can be stabilized in a strong acid medium. The observed bulk spin densities of 0.18 – 0.23 spins ½ per donor molecule in TDIAB-$PF_6$ and HDMAB-$PF_6$ solids are significant comparing to the diamagnetic properties normally obtained in solids of simple cationic salts of planar organic donor molecules. The results imply that a small degree of molecular spin separation due to the steric effect can readily increase sharply the paramagnetic spin density of solids.

### Acknowledgment

We are grateful to the National Science Foundation for financial support (Grant DMR 88-22532).

### References

1. L. Y. Chiang, D. C. Johnston, D. P. Goshorn and A. N. Bloch, *Synth. Met.*, **27**, B639 (1988).
2. L. Y. Chiang, D. C. Johnston, D. P. Goshorn and A. N. Bloch, *J. Am. Chem. Soc.*, **111**, 1925 (1989).
3. L. Y. Chiang and H. Thomann, *J. Chem. Soc., Chem. Commun.*, 172 (1989).
4. L. Y. Chiang, to be published.
5. H. J. Backer and V. D. Baan, *Rec. Trav. Chim.*, **56**, 1175 (1937).
6. F. Effenberger, E. Auer and P. Fischer, *Chem. Ber.*, **103**, 1440 (1970).
7. J. Thomaides, P. Maslak and R. Breslow, *J. Am. Chem. Soc.*, **110**, 3970 (1988).