Synthesis and EPR characterisation of [3-(*N*-ylooxy-*tert*-butylamino)-5-*tert*-butylphenyl]phenylcarbene with a quartet ground state

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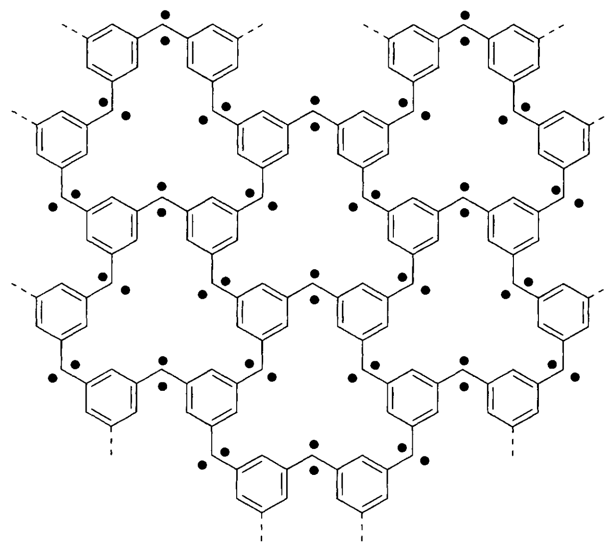
[3-(*N*-ylooxy-*tert*-butylamino)-5-*tert*-butylphenyl]-phenylcarbene, a potential new spin/magnetic coupling unit for extended spin systems, is designed, synthesized and found by EPR spectroscopy to have a quartet ground state.

Connection of free radical centres via *m*-phenylene and/or benzene-1,3,5-triyl groups has been successfully used to construct high-spin organic molecules and is considered to be one of the promising strategies for the construction of photogenerated organic ferromagnets. Nonacarbene with nonadecet ($S = 9$) ground state[1] forms a notable landmark in the approaches to carbene network **1**, a long-range goal of such studies. Construction of the oligomeric unit structures becomes more difficult as the number of units increases.[2] More recently another strategy of forming extended systems of well-defined dimensionality by coordination of triplet dinitroxide and quartet trinitroxide radicals with magnetic metal ions proved to be useful in ordering the 2p spins of the former and the 3d spins of the latter in a ferrimagnetic fashion.[3] A 2:3 complex from a quartet trinitroxide radical and bis(hexafluoroacetylacetonato)-manganese(II) showing a magnetic transition temperature of 46 K is a typical example.[3e] Here we report the synthesis of the title compound **2** which has two different kinds of spins: a triplet carbene capable of being generated photochemically and a nitroxide radical capable of forming complexes with magnetic metal ions. The heterogeneous spins are designed to couple strongly in a ferromagnetic fashion within the ligand molecule of **2**. The *tert*-butyl group on the benzene ring has been introduced to stabilize the nitroxide radical kinetically.[4]



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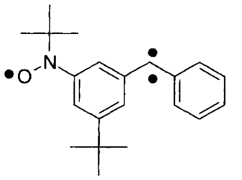

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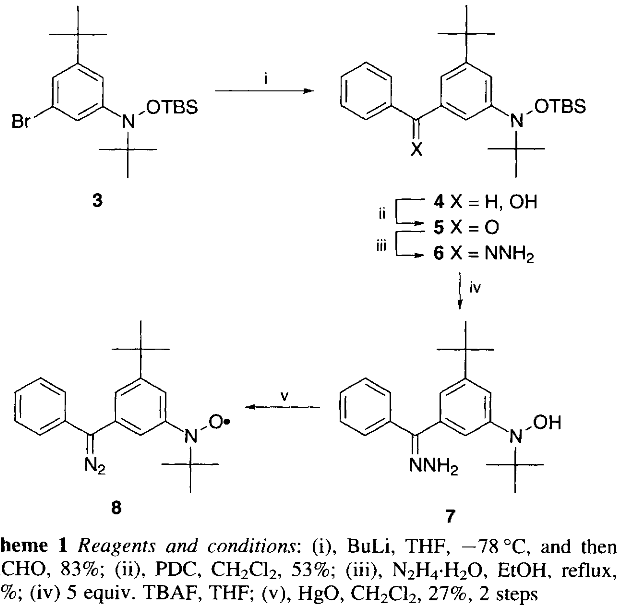
3,5-Dibromo-*tert*-butylbenzene was synthesized from *tert*-butyl benzene and converted to *N*-(3-bromo-5-*tert*-butylphenyl)-*N*-(*tert*-butyldimethylsiloxy)-*tert*-butylamine **3**.[4] The monobromo compound **3** was lithiated and treated with benzaldehyde to give alcohol **4**† which was then oxidized with pyridinium dichromate to give ketone **5**.† Treatment of **5** with hydrazine monohydrate gave hydrazone **6**† which was deprotected by treatment with tetrabutylammonium fluoride and then oxidized by yellow mercury oxide to give {3-(*N*-ylooxy-*tert*-butylamino)-5-*tert*-butylphenyl}phenyldiazomethane **8**.† In the last oxidation step, both the hydrazone and hydroxylamine groups were oxidized to the diazo and nitroxide groups, respectively.

The diazo compound **8** was confirmed by IR and EPR spectroscopy and by elemental analysis. An absorption of the diazo group was observed at 2039 cm^{-1}. The EPR spectrum of **8** consisted of three quartets at 178.3 K. The hyperfine couplings with one nitrogen ($a_N = 12.3$ G) and two *ortho* and one *para* hydrogen ($a_{\text{ortho-H}} = a_{\text{para-H}} = 2.0$ G) were determined by simulation. An EPR spectrum with a hyperfine structure of nitrogen with random orientation in solid solution was obtained at 8.3 K.

Photolysis of **8** in 2-methyltetrahydrofuran (MTHF) solid solution was performed at 8.1 K in an EPR cavity and irradiated with light from a high pressure mercury lamp attached with a sharp-cut filter ($\lambda > 480$ nm). The EPR spectrum after



Scheme 1 *Reagents and conditions*: (i), BuLi, THF, −78 °C, and then PhCHO, 83%; (ii), PDC, CH_2Cl_2, 53%; (iii), $N_2H_4{\cdot}H_2O$, EtOH, reflux, 81%; (iv) 5 equiv. TBAF, THF; (v), HgO, CH_2Cl_2, 27%, 2 steps

photolysis showed a set of fine structure lines characteristic of quartet species (Fig. 1). The spectrum resembled closely that of the monoanion of *m*-phenylenebis(phenylmethylene) **10**, reported to have a quartet ground state.[5] Three *z* and three *xy* lines, an extra line and a forbidden band, whose assignment is shown in Fig. 1, were observed, suggesting the photolysate was in the quartet state. Two signals were observed for each of the *y* and *z* resonances but only one signal was observed for each *x*, indicating that there were two or more conformers of the quartet species present. From the signal spacing of the highest field z_3 absorptions at 619 and 634 mT and lowest field z_1 signal at 113 mT, the *D* values were obtained as 0.118 and 0.125 cm^{-1} for the two species. Approximate *E* values of 0.0035 and 0.0060 cm^{-1}, respectively, were obtained by simulation on the basis of a perturbation treatment to third order in the fine-structure energy by using the program written by Itoh *et al.*[6] These *D* values are close to that of **10**, *i.e.* 0.120 cm^{-1}.[5] While the conformation of *m*-phenylenebis(phenylmethylene) **9** is reported to be asymmetric,[7] **10** is said to have a symmetric conformation.[5] Two conformers with high and low axial symmetry may be involved in **2**. Conformational analysis remains to be carried out.

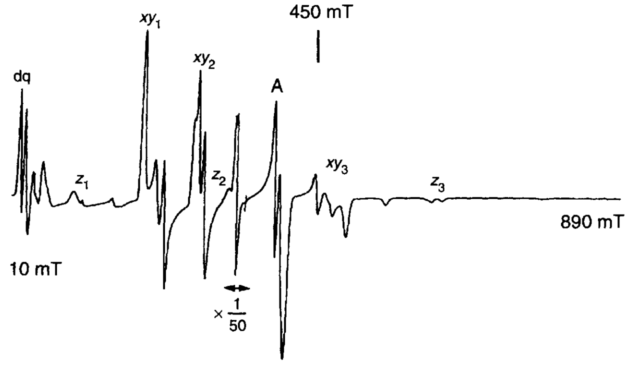
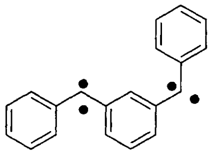


Fig. 1 EPR Spectrum of a 15 mmol dm^{-3} degassed MTHF solution of **2** at 8.1 K, (9.412 GHz): dq and A denote a forbidden band and an extra line, respectively



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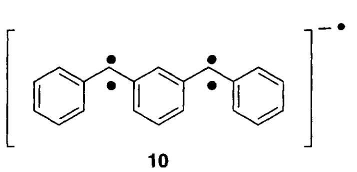

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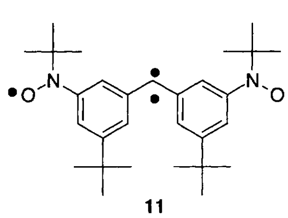

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Temperature dependence of the signal intensity due to the xy_1 transition obeyed a Curie law up to 50 K demonstrating that the quartet state was in a ground state. While **8** is a monodentate ligand and therefore no extended spin systems can be obtained, bismonodentate bridging ligands such as **11** may be used to form, with a coordinatively doubly unsaturated magnetic metal complex, polymeric paramagnets which would upon irradiation give ferri-/ferro-magnets.

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Footnote

† *Spectral data* for **4**: Pale yellow oil. IR (NaCl) ν/cm^{-1} 3370, 2959, 2930, 2899 and 2857; ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$) δ −0.19 (bs, 6 H, SiMe), 0.84 (s, 9 H, SiBu^t), 1.05 (s, 9 H, NBu^t), 1.28 (s, 9 H, Bu^t), 2.12 (d, *J* 3.9 Hz, 1 H, OH), 5.80 [d, *J* 3.9 Hz, 1 H, C*H*(OH)], 6.99 (bs, 1 H, Ar-H) and 7.16–7.37 (m, 7 H, Ar-H). For **5**: Pale yellow oil. IR (NaCl) ν/cm^{-1} 2959, 2930, 2905, 2857 and 1663; ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$) δ −0.11 (bs, 6 H, SiMe), 0.89 (s, 9 H, SiBu^t), 1.09 (s, 9 H, NBu^t), 1.34 (s, 9 H, Bu^t), 7.36 (bs, 1 H, ArH), 7.46 (t, *J* 7.3 Hz, 2 H, ArH), 7.55–7.63 (m, 3 H, ArH) and 7.79 (d, *J* 7.7 Hz, 2 H, ArH). For **6**: Pale yellow oil. IR (NaCl) ν/cm^{-1} 3401, 2959, 2928, 2857 and 1586; ^{1}H NMR (270 MHz, $\mathrm{CDCl_3}$) δ −0.19 (bs, 6 H, SiMe), −0.10 (bs, 6 H, SiMe), 0.80 (s, 9 H, SiBu^t), 0.88 (s, 9 H, SiBu^t), 1.00 (s, 9 H, NBu^t), 1.10 (s, 9 H, NBu^t), 1.29 (s, 9 H, Bu^t), 1.31 (s, 9 H, Bu^t), 5.37 (s, 2 H, $\mathrm{NNH_2}$), 5.40 (s, 2 H, $\mathrm{NNH_2}$), 6.81–7.72 (m, 16 H, ArH). For **8**: Red oil. IR (NaCl) ν/cm^{-1} 2965, 2870, 2039 and 1661; UV–VIS ($\mathrm{CH_2Cl_2}$) λ_{max} nm 520 (sh).

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