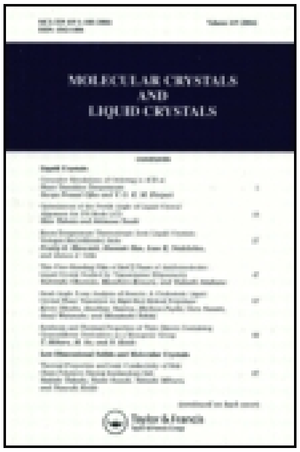


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Syntheses and Esr Characterizations of Diphenylcarbenes Carrying T-Butyl Nitroxide and Nitronyl Nitroxide Radicals as Substituents and Having Quartet Ground States

Kenji Matsuda [a] & Hizu Iwamura [a]

[a] Institute for Fundamental Research in Organic Chemistry, Kyushu University, Fukuoka, 812-81, Japan

To cite this article: Kenji Matsuda & Hizu Iwamura (1997): Syntheses and Esr Characterizations of Diphenylcarbenes Carrying T-Butyl Nitroxide and Nitronyl Nitroxide Radicals as Substituents and Having Quartet Ground States, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 306:1, 89-94

To link to this article: http://dx.doi.org/10.1080/10587259708044553

Mol. Cryst. Liq. Cryst., 1997, Vol. 306, pp. 89–94
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESES AND ESR CHARACTERIZATIONS OF DIPHENYLCARBENES CARRYING *t*-BUTYL NITROXIDE AND NITRONYL NITROXIDE RADICALS AS SUBSTITUENTS AND HAVING QUARTET GROUND STATES

KENJI MATSUDA and HIIZU IWAMURA
Institute for Fundamental Research in Organic Chemistry,
Kyushu University, Fukuoka 812-81, Japan

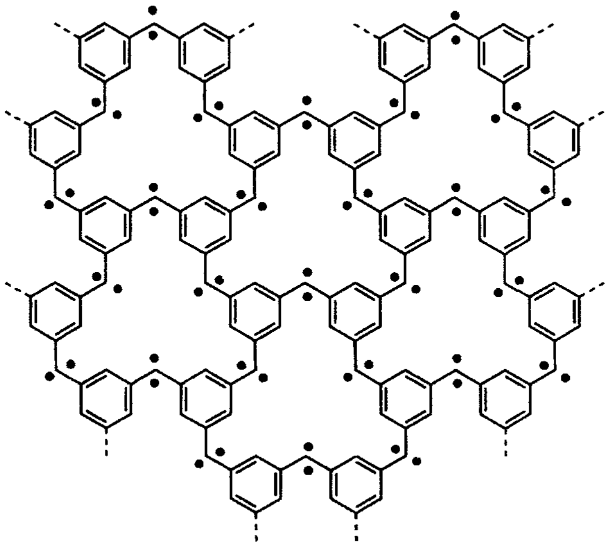
Abstract Diphenylcarbenes possessing *t*-butyl nitroxide (**2**) and nitronyl nitroxide (**3**) radicals, potential new spin/magnetic coupling units for extended spin systems, were designed, synthesized, and characterized by ESR spectroscopy. The ESR spectrum of **2** indicated the existence of different conformers, while **3** had only one conformer. These carbenes had quartet ground states determined from the fine structures and the temperature dependence of the signals.

INTRODUCTION

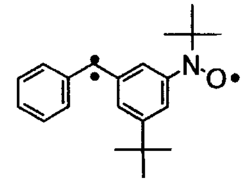
Connection of free radical centers via ferromagnetic coupling units has been successfully used to construct high-spin organic molecules[1-3] and is considered to be one of the promising strategies for eventual construction of magnetic images by irradiation.[4-6] Nonacarbene with a nonadecet ($S = 9$) ground state forms a notable landmark in the approaches to carbene network **1** serving as a long-range goal of such studies.[5] Construction of the oligomeric unit structures by organic synthesis however becomes increasingly difficult as the number of the units increases.[6]

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.[7]

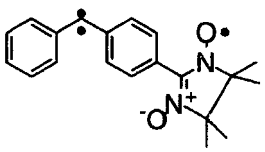
We now report the syntheses of the diphenylcarbenes possessing *t*-butyl nitroxide **2** and nitronyl nitroxide **3** which have two different kinds of spins[8]: a triplet carbene capable of being generated photochemically and a nitroxide radical feasible of forming complexes with magnetic metal ions. The heterogeneous spins are designed on the basis of topological symmetry to couple strongly in a ferromagnetic fashion within the molecules of **2** and **3**.



1



2

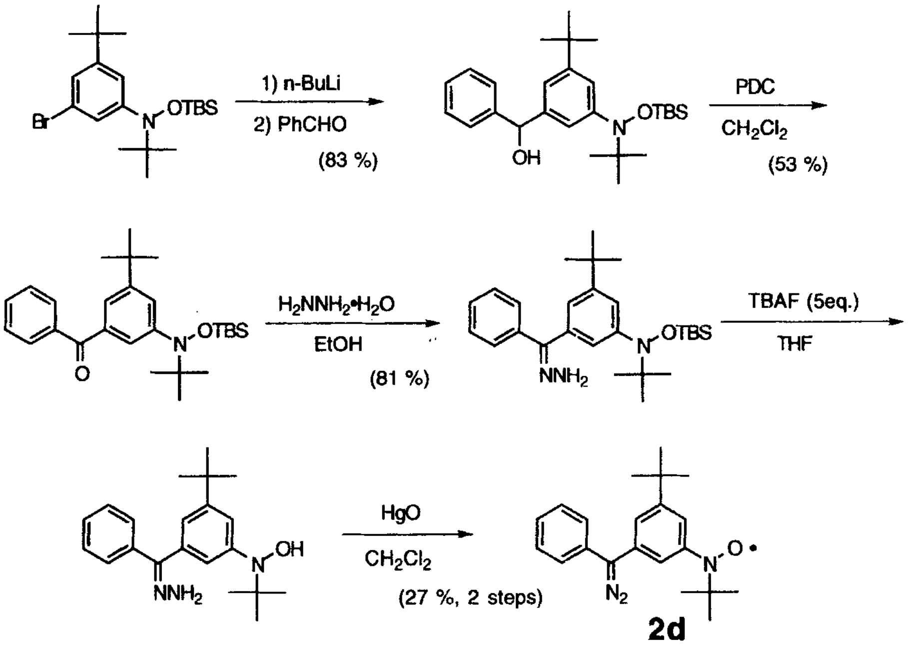


3

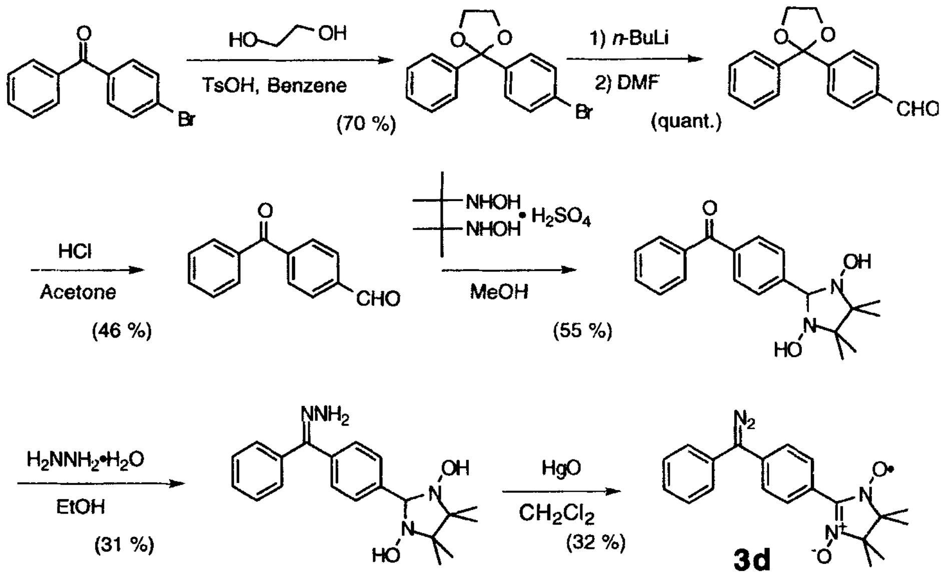
MOLECULAR DESIGN AND PREPARATION OF THE PRECURSORS

These carbenes were generated by the photolysis of the corresponding diazo compounds. The synthetic routes to the diazo compound **2d** were described in Scheme 1. The synthesis was facilitated by using the *t*-butyldimethylsiloxy protecting group.[9] In the last oxidation step, both the hydrazone and hydroxylamine groups were oxidized simultaneously to the diazo and nitroxide groups, respectively. The diazo compound **2d** was obtained as red solid showing an IR absorption at 2039 cm^{-1} and a UV-vis absorption at 520 (sh) nm . An ESR spectrum of **2d** consisted of three sets of quartet lines at 178.3 K. The hyperfine couplings with one nitrogen (a_N = 12.3 G) and two ortho and one para hydrogens ($a_{\text{ortho-H}} = a_{\text{para-H}}$ = 2.0 G) were determined by simulation. An ESR spectrum with a hyperfine structure of nitrogen with random orientation in solid solution was obtained at 8.3 K.

To the diazo compound **3d**, the synthesis was performed according to the Scheme 2. The simultaneous oxidation was also performed to get the nitronyl nitroxide and the diazo moieties. The diazo compound **3d** was confirmed by IR and ESR spectra. The IR absorption of the diazo group was observed at 2039 cm^{-1}. UV-vis absorptions were observed at 550 (sh), 607 (800), 645 (840), and 720 (sh) nm. An ESR spectrum of **3d** measured at 174 K consisted five lines with hyperfine coupling with two equivalent nitrogens (a_N = 7.4 G)



SCHEME 1 Synthetic Scheme to the diazo compound **2d**



SCHEME 2 Synthetic Scheme to the diazo compound **3d**

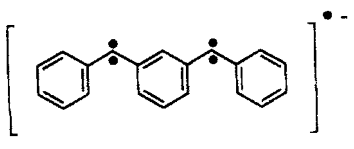
PHOTOLYSIS AND ESR SPECTRA

Photolysis of **2d** in 2-methyltetrahydrofuran (MTHF) solid solution was performed at 8.1 K in an ESR cavity. Light from high pressure mercury lamp attached with a sharp-cut filter ($\lambda > 480$ nm) was irradiated. An ESR spectrum after photolysis are shown in Figure 1. The spectrum resembled closely that of the monoanion of *m*-phenylenebis(phenylmethylene) **4** , reported to be with quartet ground state.[10] Three z and three xy lines and extra line and forbidden band was assigned, suggesting the photolysate was with quartet state. 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 a ground state.

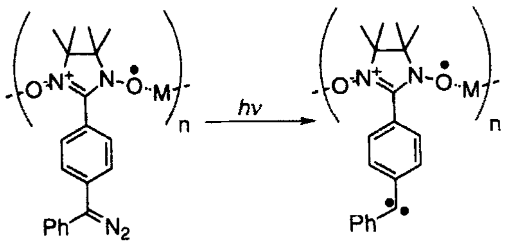
Two signals were observed for each of the y and z resonances but one signals for each of x, indicating that there were two or more conformers of the quartet species present. From the signal spacing of the highest field z_3 resonances at 619 and 634 mT and lowest field z_1 signal at 113 mT, the D values 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 a program written by Itoh et al.[11] These D values are close to that of **4**, i.e., 0.120 cm^{-1}.[10] Two conformers with high and low axial symmetry may be involved in **2**. Further conformational analysis remains to be carried out.

The ESR spectrum of the photoproduct of **3d** shown in Figure 2 also has a quartet fine structure assigned to the carbene **3**. In the case of the carbene **3**, the one conformer was observed: $D = 0.113$ cm^{-1}, $E = 0.006$ cm^{-1}. Because the nitronyl nitroxide has symmetric shape, the possible conformation is only one.

While **2** is a monodentate ligand and therefore no extended spin systems can be obtained, the nitronyl nitroxide **3** is a bis(monodentate) ligand and so may be used to form, with coordinatively doubly unsaturated magnetic metal complex, polymeric meta- or ferrimagnets.[7] Their magnetic properties would upon irradiation be strengthened or weakened by coupling with the pendant carbenes in **6**.



4



5 **6**

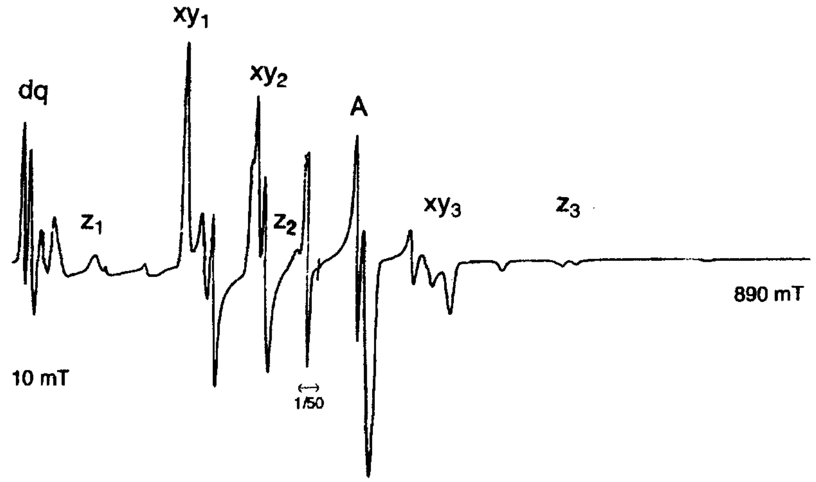


FIGURE 1 ESR Spectrum of the carbene **2** at 8.1 K (9.412 GHz).

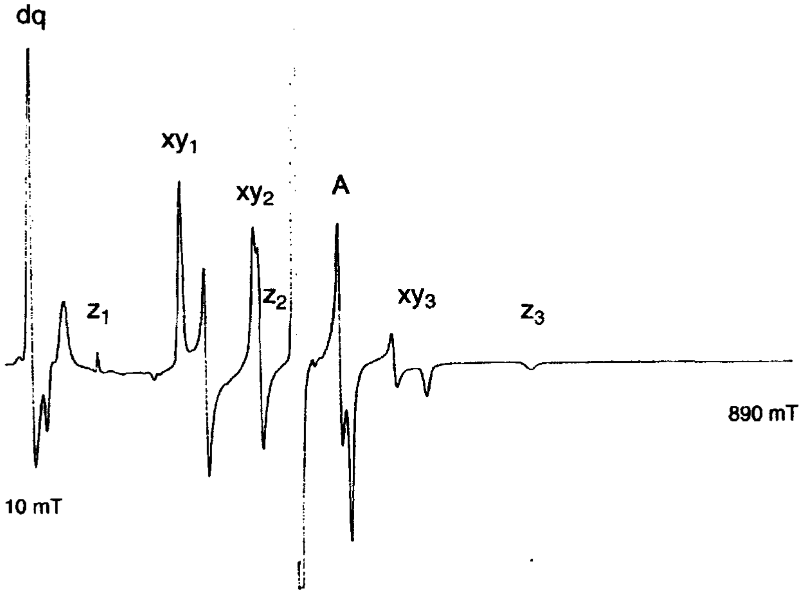


FIGURE 2 ESR Spectrum of the carbene **3** at 6.3 K (9.406 GHz).

REFERENCES

1. For reviews see: (a) H. Iwamura, Adv. Phys. Org. Chem., 26, 179 (1990). (b) D. A. Dougherty, Acc. Chem. Res., 24, 88 (1991). (c) H. Iwamura and N. Koga, Acc. Chem. Res., 26, 346 (1993). (d) H. Kurreck, Angew. Chem., Int. Ed. Engl., 32, 1409 (1993). (e) J. S. Miller and A. J. Epstein, Angew. Chem., Int. Ed. Engl., 33, 385 (1994). (f) A. Rajca, Chem. Rev., 94, 871 (1994). (g) J. S. Miller and A. J. Epstein, Chem. Eng. News, Oct. 2, 30 (1995). (h) P. S. Zuev and R. S. Sheridan, Tetrahedron, 51, 11337 (1995).
2. Perchloropolyarylmethyl: (a) J. Veciana, C. Rovira, M. I. Crespo, O. Armet, V. M. Domingo and F. Palacio, J. Am. Chem. Soc., 113, 2552 (1991). (b) J. Veciana, C. Rovira, N. Ventosa, M. I. Crespo and F. Palacio, J. Am. Chem. Soc., 115, 57 (1993).
3. Polyarylmethyl: (a) A. Rajca, J. Am. Chem. Soc., 112, 5890 (1990). (b) A. Rajca, S. Utamapanya and J. Xu, J. Am. Chem. Soc., 113, 9235 (1991). (c) A. Rajca, S. Utamapanya and S. Thayumanavan, J. Am. Chem. Soc., 114, 1884 (1992). (d) A. Rajca and S. Utamapanya, J. Am. Chem. Soc., 115, 2396 (1993). (e) A. Rajca, S. Rajca and R. Padmakumar, Angew. Chem., Int. Ed. Engl., 33, 2091 (1994). (f) A. Rajca, S. Rajca and S. R. Desai, J. Am. Chem. Soc., 117, 806 (1995).
4. (a) N. Mataga, Theor. Chim. Acta., 10, 372 (1968). (b) K. Itoh, Chem. Phys. Lett., 1, 235 (1967). (c) E. Wasserman, R. W. Murray, W. A. Yager, A. M. Trozzolo and G. Smolinsky, J. Am. Chem. Soc., 89, 5076.
5. (a) I. Fujita, Y. Teki, T. Takui, T. Kinoshita, K. Itoh, F. Miko, Y. Sawaki, H. Iwamura, A. Izuoka, and T. Sugawara, J. Am. Chem. Soc., 112, 4074 (1990). (b) N. Nakamura, K. Inoue, H. Iwamura, T. Fujioka, and Y. Sawaki, J. Am. Chem. Soc., 114, 1484 (1992). (c) K. Furukawa, T. Matsumura, Y. Teki, T. Kinoshita, T. Takui, and K. Itoh, Mol. Cryst. Liq. Cryst., 232, 251 (1993). (d) N. Nakamura, K. Inoue, and H. Iwamura, Angew. Chem. Int. Ed. Engl., 32, 872 (1993). (e) K. Matsuda, N. Nakamura, K. Takahashi, K. Inoue, N. Koga, and H. Iwamura, J. Am. Chem. Soc., 117, 5550 (1995).
6. (a) K. Matsuda, N. Nakamura, K. Inoue, N. Koga, and H. Iwamura, Chem. Eur. J., 2, 259 (1996). (b) K. Matsuda, N. Nakamura, K. Inoue, N. Koga, and H. Iwamura, Bull. Chem. Soc. Jpn., 69, 1483 (1996). (c) K. Matsuda, N. Nakamura, K. Takahashi, K. Inoue, N. Koga, and H. Iwamura, "Molecular-Based Magnetic Materials", ACS Symposium Series, in press.
7. (a) C. Benelli, A. Dei, D. Gatteschi, H. U. Gudel, and L. Pardi, Inorg. Chem., 28, 3089 (1989). (b) H. O. Stumpf, L. Ouahab, Y. Pei, D. Grandjean, O. Kahn, Science, 261, 447 (1993). (b) K. Inoue and H. Iwamura, J. Am. Chem. Soc., 116, 3173 (1994). (c) K. Inoue and H. Iwamura, J. Chem. Soc., Chem. Commun., 2273 (1994). (d) K. Inoue, T. Hayamizu, and H. Iwamura, Chem. Lett., 745 (1995). (e) K. Inoue, T. Hayamizu, H. Iwamura, D. Hashizume, and Y. Ohashi, J. Am. Chem. Soc., 118, 1803 (1996).
8. For the *t*-butylnitroxide carbene: K. Matsuda and H. Iwamura, J. Chem. Soc., Chem. Commun., 1131, (1996).
9. T. Ishida and H. Iwamura, J. Am. Chem. Soc., 113, 4238 (1991).
10. (a) M. Matsushita, T. Momose, T. Shida, Y. Teki, T. Takui, and K. Itoh, J. Am. Chem. Soc., 112, 4700 (1990). (b) M. Matsushita, T. Nakamura, T. Momose, T. Shida, Y. Teki, T. Takui, T. Kinoshita, and K. Itoh, J. Am. Chem. Soc., 114, 7470 (1992). (c) M. Matsushita, T. Nakamura, T. Momose, T. Shida, Y. Teki, T. Takui, T. Kinoshita and K. Itoh, Bull. Chem. Soc. Jpn., 66, 1333 (1993).
11. Y. Teki, T. Takui, H. Yagi, K. Itoh, and H. Iwamura, J. Chem. Phys., 83, 539 (1985). Due to the approximation used in the simulation, the *E* values have to be taken as preliminary.