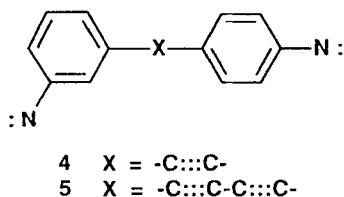


Fig 1

obtained by low-temperature photolysis of **2** in Fluorolube and in 1–5 wt% poly(methyl methacrylate) films cast from dichloromethane solution.

The ESR spectrum of **1** in Figure 1 shows the following resonances: *ca* 750 (broad, indistinct), 1653, 3012 (strong, sharp), 3840 (broad), 6029, 6683, 6920 and 8350 G (weak). The two resonances at 6683 and 6920 G match well the positions of mononitrene peaks produced by comparison photolyses of *m*- and *p*-biphenylazide, respectively; these values correspond to zero-field splitting  $|D/hc|$  values of 0.88 and 0.97  $\text{cm}^{-1}$  respectively (these mononitrenes have been described previously<sup>5</sup>), with  $|E/hc|$  being essentially zero. The dinitrene set of resonances resemble those of Iwamura and Murata's<sup>6</sup> alkyne-linked quintet GS dinitrenes **4** and **5**, described in the single other study of



Scheme 1

linking two phenylnitrenes in different connectivities by conjugating groups. The similarity of our spectrum to these others supports our conclusion that **1** is indeed a quintet state dinitrene. There is also a similarity to the monocyclic quintet dinitrene 1,3-phenylenedinitrene, whose ESR spectrum was checked by us and was first

described by Wasserman *et al.*<sup>7</sup> Although formally a cousin of **4–5** by connectivity theory, this species is different in having two nitrenes conjugated through a single ring, rather than constituting a test of two open-shell systems linked by a conjugated group. If we assign the quintet H-1 resonance to 8360 G, use of perturbation methods<sup>7</sup> leads to an ESR zero-field splitting value of  $|D/hc| = 0.153 \text{ cm}^{-1}$ . If we assume like Iwamura and Murata<sup>6</sup> and Wasserman *et al.*<sup>7</sup> that the H-2 resonance is hidden under mononitrene resonances at *ca* 6700 and *ca* 6900 G, we find  $|E/hc| = 0.019 \text{ cm}^{-1}$ . The spectrum in MeTHF is remarkably clean, and shows little radical impurity in the  $g \approx 2$  region (3300–3500 G).

We tested whether the quintet is the ground state of **1** by preparation of a Curie law plot of ESR spectral intensity vs reciprocal of absolute temperature, using the strong quintet peak at 3012 G for the plot. All spectra were obtained on an APD Cryogenic Displex closed-cycle circulating helium cryostat, with a copper sample spindle and Suprasil outer vacuum shroud to allow photolysis; temperatures were measured with a gold–chromel thermocouple attached to the sample spindle. Spectral peak intensities were measured by double integration of the standard derivative ESR spectrum, using two different methods as a check of results. Over the range 10–70 K, we found excellent linearity, with a correlation coefficient of 0.99 (Figure 2). At temperatures  $> 80 \text{ K}$ , the spectrum of **1** decays irreversibly, even in poly(methyl methacrylate); thawing to room temperature of the sample and recooling shows no residual ESR peaks. Although these results do not strictly prove that **1** has a quintet GS (the difficulties of

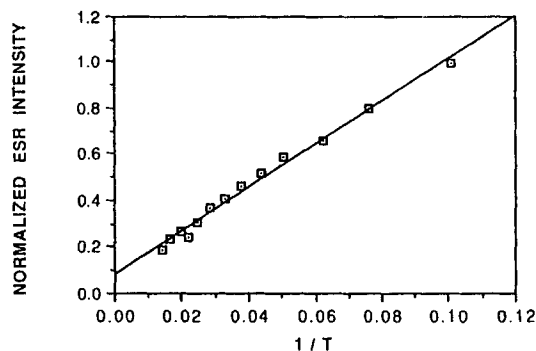


Fig 2

interpreting a linear Curie plot have been well set forth by Berson<sup>8</sup>), the most likely interpretation of results supports this assertion.

The finding of a high-spin ground state for **1** is in accord with the qualitative expectations of various connectivity-based theories,<sup>9-14</sup> which do not necessarily, however, take explicitly into account the effects upon ground-state multiplicity of possible non-planar conformers or of heteroatom  $\pi$ -isoelectronic substitutions. This finding is also consistent with the computational studies by us indicating that even a twisted dinitrene **1** is expected to favor a quintet ground state. We have previously shown that semi-empirical molecular orbital plus configuration interaction computations give ground-state (GS) spin multiplicity predictions in accord with experimental findings and with more rigorous *ab initio* computational predictions. We find by use of Dewar's AM1<sup>15</sup> method with configuration interaction<sup>16-19</sup> that a coplanar geometry of **1** favors a quintet GS by about 9 kcal mol<sup>-1</sup>, while a 90° twisted geometry still favors the quintet by about 4 kcal mol<sup>-1</sup>. This is a remarkable demonstration of the strength of the 3,4'-biphenyl group in ferromagnetically coupling the two spin-bearing nitrene sites, despite decreased overlap in the twisted geometry.

Itoh and co-workers<sup>20,21</sup> studied in some detail a 3,3'-dicarbene connectivity isomer of our system, biphenyl-3,3'-bis(phenylmethylene), which was found to have a singlet ground state in agreement with valence bond<sup>9-12</sup> predictions. A Russian group<sup>22</sup> has photolysed the bisdiaz precursor to biphenyl-4,4'-bis(phenylmethylene) and obtained triplet ESR signals. Our study of quintet **1** now shows the ferromagnetic nature of the 3,4'-biphenyl connectivity in exchange coupling, with use of nitrene spin-bearing sites rather than carbenes. The dicarbene systems are conformationally more complex than dinitrene **1**, hence we consider the geometric simplification in this and other dinitrenes to be in some ways preferable for studies of exchange coupling.

Our experimental data do not unequivocally show

whether **1** is planar or not, since despite that fact that biphenyl itself generally has a dihedral torsional angle of 35° between rings with a low rotational energy barrier,<sup>23,24</sup> this may not apply to the dinitrene itself. The similarity of our  $|D/hc|$  value for **1** to that for planar **4**, which has<sup>6</sup>  $|D/hc| = 0.1575$  cm<sup>-1</sup> and  $|E/hc| = 0.020$  cm<sup>-1</sup>, may indeed imply that **1** is planar or time-averaged planar, as **4** and **5** were believed to be despite their lack of conformational constraint. We hope to synthesize derivatives of **1** where more torsion is mandatory, in an effort to see if the spectral  $|D/hc|$  value is altered in a manner consistent with any dramatic change in the degree of exchange interaction relative to **1**.

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