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Zero-field splitting parameters of quintet 2,6-dinitrenopyridines

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ABSTRACT: The zero field splitting parameters of two 2,6-dinitrenopyridines were estimated to be $|D/hc| \cong 0.19$–$0.20\,\mathrm{cm}^{-1}$ and $|E/hc| \cong 0.064$–$0.066\,\mathrm{cm}^{-1}$ by lineshape simulation of frozen solution X-band ESR spectra. This large ratio of $|E/D|$ is consistent with a dominating dipolar interaction between the two nitrene units having a relative interaction vector angle of about $114°$–$116°$. UB3LYP/6-31G* computations of 2,6-dinitrenopyridine predict a very similar interaction vector angle. These results are quite different from analogous results observed for *meta*-dinitrenobenzenes. The experimental zero-field splitting (zfs) and computational results indicate that the ESR spectroscopy of 2,6-dinitrenopyridines are dominated by the one-center interactions between unpaired electrons on the nitrene units (the triplet mononitrene zfs), and the relative geometry of interaction between the mononitrenes caused by the molecular geometry of the dinitrenopyridine (the interaction vector angle). Copyright © 2006 John Wiley & Sons, Ltd.

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KEYWORDS: nitrene; dinitrene; zero field splitting; electron spin resonance; electron paramagnetic resonance; dipolar splitting; open shell molecules

INTRODUCTION

Interest in modeling electron–electron exchange interactions in organic magnetic materials[1,2], has led to much effort[3] to examine the electronic properties of high-spin dinitrenes, especially by electron spin resonance (ESR) spectroscopy. Quintet dinitrenes **1** and **2** with interaction vector angles θ between two nitrene C—N bonds of about 0 or 180° display rather simple ESR spectra that indicate formation of quintet spin-states with zero-field splitting (zfs) parameters of $|D/hc| = 0.24$–$0.29\,\mathrm{cm}^{-1}$ and $|E/hc| = 0.001$–$0.009\,\mathrm{cm}^{-1}$.[4,5] Another type of ESR spectrum has been observed for numerous quintet dinitrenes with fixed *meta*-orientation of two nitrene units in the aromatic ring (*meta*-dinitrenes such as **3**) and vector angles $\theta \cong 120°$.[6–14] These spectra typically show two signals of medium intensity at 800–1200 and 1300–

1600 G, a major signal at 2800–3100 G and various weak signals in the region from 3400 to 10 000 G. Quintet spin-states of this type have been reported to have $|D/hc| = 0.18$–$0.21\,\mathrm{cm}^{-1}$ and $|E/hc| = 0.030$–$0.042\,\mathrm{cm}^{-1}$,[6–14] with more recent estimates being based[11,12,14] on spectral lineshape simulations.

In this work, we describe simulation and analysis of ESR spectra of quintet dinitrenes produced during the photolysis of diazides **4a,b** in cryogenic matrices, which incorporate heteroaromatic 2,6-pyridindiyl as an exchange linker between the nitrene units. The ESR spectra from these experiments appear to be characteristic of quintet 2,6-dinitrenopyridine systems.[14] The present analysis indicates that the zfs parameters of such systems are consistent with effective interaction vector angles of $\theta \cong 114°$–$115°$, based on application of the inter-nitrene dipolar interaction model that has been successfully applied[4,5,11] to systems **1**–**3**.
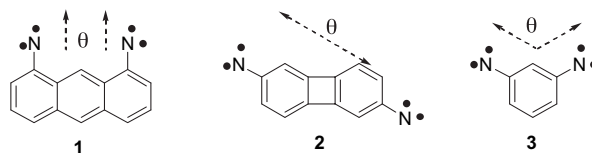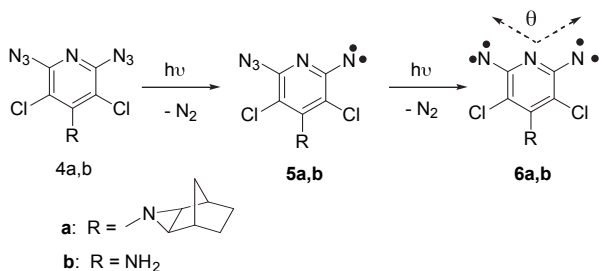
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RESULTS

The syntheses of diazides **4a**[15] and **4b**[16] have been described elsewhere. The photolysis of diazide **4a** in a degassed frozen 2-methyltetrahydrofuran (2MTHF) solution for 5 min with a xenon lamp (Pyrex filtered, >300 nm) at 77 K gave an X-band ESR spectrum displaying signals at 390, 3320, 3420, 3700, 6740, 7001, and 9500 G (Fig. 1a). A similar ESR spectrum showing signals at 320, 3390, 3470, 3760, 7000, 7340, and 9890 G was obtained after the photolysis of diazide **4b** under the same conditions (Fig. 2a). We previously reported the spectra derived from **4a,b** without detailed zfs analysis.[14] Notably, the 0–4000 G regions differ
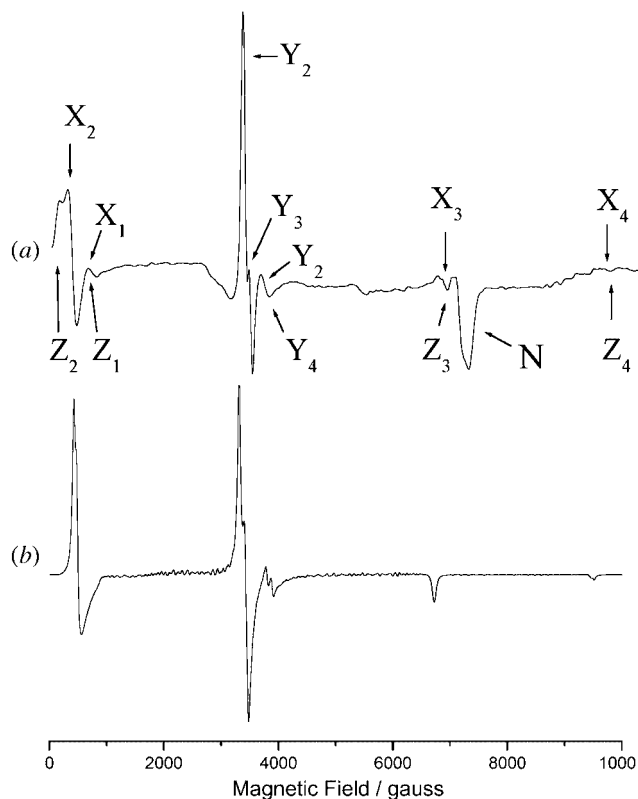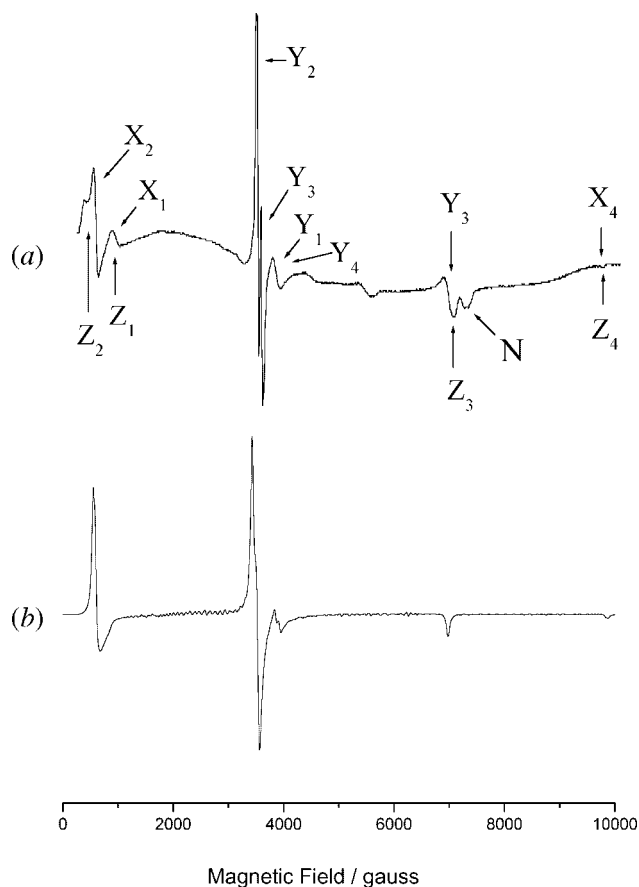

Figure 2. (a) ESR spectrum from the photolysis of diazide **4b** ($v_0 = 9.607$ GHz) at 77 K in 2-methyltetrahydrofuran glass. (b) Simulated ESR spectrum for a randomly oriented quintet spin-state with $g = 2.0023$, $|D/hc| = 0.2020$ cm^{-1} and $|E/hc| = 0.0664$ cm^{-1}. N shows the signal of triplet **5b**, peaks labeled with X, Y, Z are assigned to quintet **6b**

significantly from ESR spectra for numerous previously studied quintet dinitrenes,[4–14] although comparison to previous spectra supports peak assignments at about 7000 G to triplet azidonitrenes **5a,b** with other peaks attributable to quintet dinitrenes **6a,b**.

DISCUSSION

According to theory[17] for ESR spectra of quintet states, five energy sublevels W_{-2}, W_{+2}, W_{-1}, W_{+1}, W_0 (Fig. 3a) and up to 12 lines can be present, 4 X-, 4 Y-, and 4 Z-transitions. Figure 3b shows a generic, first order spectrum having modest linewidths where $|E/hc| > 0$ cm^{-1}. For quintets with $|E/hc| = 0$ cm^{-1}, the theoretical number of lines will decrease from 12 to 8 due to the lack of splitting between the X- and Y-transitions, as shown in Fig. 3c. Moreover, when the zfs is large enough, some of these lines will not appear[11] in the experimentally accessible 0–10 000 G magnetic field range of standard X-band ESR spectrometers. For

Figure 1. (a) ESR spectrum from the photolysis of diazide **4a** ($v_0 = 9.562$ GHz) at 77 K in 2-methyltetrahydrofuran glass. (b) Simulated ESR spectrum for a randomly oriented quintet spin-state with $g = 2.0023$, $|D/hc| = 0.191$ cm^{-1} and $|E/hc| = 0.0625$ cm^{-1}. N shows the signal of triplet **5a**, peaks labeled with X, Y, Z are assigned to quintet **6a**
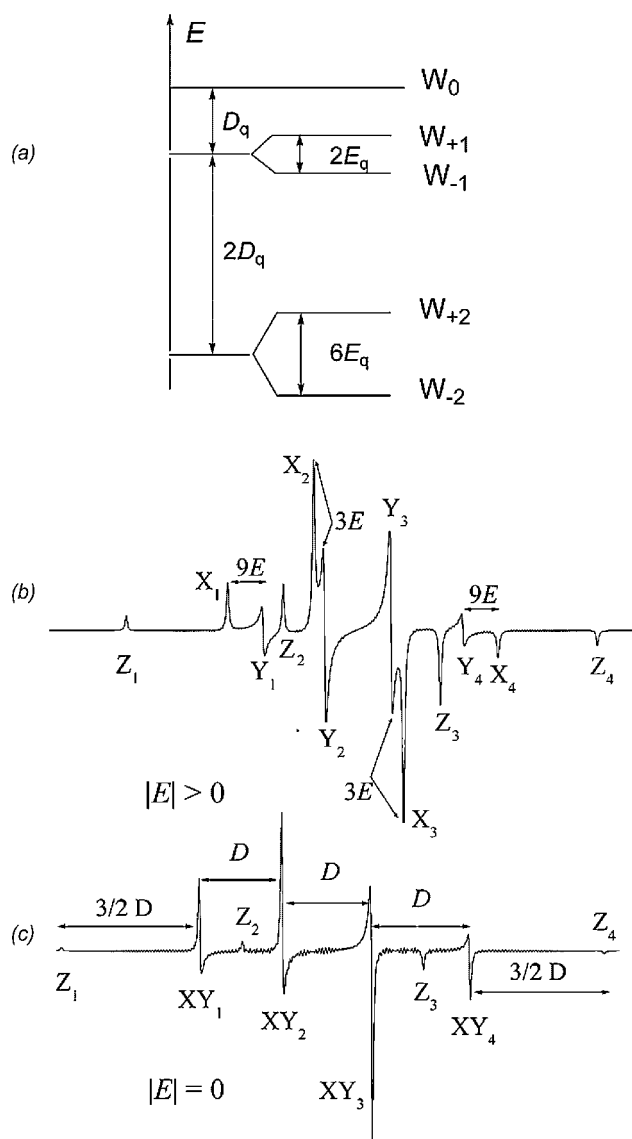
Figure 3. (a) Energy sublevels for quintet spin-states. (b) A first-order ESR spectrum for a randomly oriented quintet spin-state with $|D/E| = 20$. (c) A first-order ESR spectrum for a randomly oriented quintet spin-state with $|E/hc| = 0$

instance, the experimental ESR spectrum of quintet dinitrene **2** with $|D/hc| = 0.260 \, \text{cm}^{-1}$ and $|E/hc| = 0.0005 \, \text{cm}^{-1}$ shows only six quintet-assignable signals at 650 (Z), 965 (X,Y), 2640 (X,Y), 3770 (Z), 5680 (off-resonance peak), and 7600 G (X,Y).[5] By comparison, the fixed geometry *meta*-connectivity quintet phenylenedinitrenes can all readily be recognized by two indicative[6–15] ESR spectral features: (i) a small number of strong signals and (ii) a major signal at ~2400–3000 G. But, if a dinitrene has $E_q \sim 1/3 \, D_q$, the X- and Y-transitions in Fig. 3 can overlap with Z-transitions, reducing the resolved number of signals in the ESR spectrum.

As mentioned above, lineshape simulation of dinitrene spectra has been very important to assist estimation of their zfs parameters. The simulated zfs of fixed geometry

meta-connectivity quintet dinitrenes is best understood[11] in terms of the dipolar interaction model first described by Wasserman[6] and Itoh,[18] whereby the quintet zfs D_q and E_q values are determined primarily by the vector angle θ and by the zfs D_t values of the nitrene units that yield the quintet state. This relationship is given by Eqns (1) and (2), where $\alpha = (\theta/2)$; these equations assume that $|D_t| \gg |E_t|$ and that the dipolar exchange interaction between nitrene units is much smaller than analogous exchange between unpaired spin density regions upon each nitrene unit.

$$D_q = \frac{D_t(3 \sin^2 \alpha - 1)}{6} \tag{1}$$

$$E_q = \frac{D_t(\cos^2 \alpha)}{6} \tag{2}$$

D_t of the nitrene components of quintet dinitrenes should be essentially that of the corresponding triplet azidoarylnitrenes, typically[20] about $1.00 \, \text{cm}^{-1}$. Where D_t is known, θ can be compared to reasonable dinitrene geometric values by simulating the quintet lineshape from zfs parameters using Eqns (1) and (2). Figures 1b and 2b show lineshape simulations obtained using the SIM program of Weihe for simulation of electron spin resonance spectra.[19] The program uses iterative diagonalization of exact spin Hamiltonians to locate resonance magnetic fields, and is described elsewhere.[19] The estimated quintet zfs parameters for **6a** are $|D_q/hc| = 0.191 \, \text{cm}^{-1}$, $|E_q/hc| = 0.0625 \, \text{cm}^{-1}$, and for **6b** are $|D_q/hc| = 0.202 \, \text{cm}^{-1}$, $|E_q/hc| = 0.0664 \, \text{cm}^{-1}$. Using the same methodology for the triplet azidonitrenes: **5a** has $|D_t/hc| = 1.029 \, \text{cm}^{-1}$, $|E_t/hc| < 0.003 \, \text{cm}^{-1}$, and **5b** has $|D_t/hc| = 1.068 \, \text{cm}^{-1}$, $|E_t/hc| < 0.002 \, \text{cm}^{-1}$. The mononitrene zfs are in good accord with literature precedents.[20]

In order to help further assign the signals in the quintet dinitrene ESR spectra for **6a,b**, calculations of separate $W_{\pm 1}/W_0$ (Fig. 4a) and $W_{\pm 2}/W_{\pm 1}$ transitions (Fig. 4b) were carried out. These assignments can be useful for spectral identification of quintet dinitrenes, since it is very difficult to assign zfs precisely for these species without higher field spectral acquisition, given the small number of intense spectral bands. Both $W_{\pm 2}/W_{\pm 1}$ and $W_{\pm 1}/W_0$ calculations give three transitions. For the $W_{\pm 2}/W_{\pm 1}$ transitions, the central line at 3700 G is attributable to overlapping Y_1 and Y_4 transitions, while two outer lines at 400 and 9500 G result from overlapping of Z_1/X_1 and Z_4/X_4 transitions. Due to considerable deviation of the spectrum from first-order behavior, the signals are not symmetrical about the central frequency. For the $W_{\pm 1}/W_0$ transitions, the central lines at ~3400 G are slightly split into separate Y_2 and Y_3 transitions, the X_2-transition overlaps with the Z_1-, Z_2-, and X_1-transitions at 400 G, and the X_3 transition overlaps with the Z_3 transition at 6740 G.

Using the experimental triplet zfs for **5a,b** to provide D_t for Eqns (1) and (2), the zfs parameters derived for the
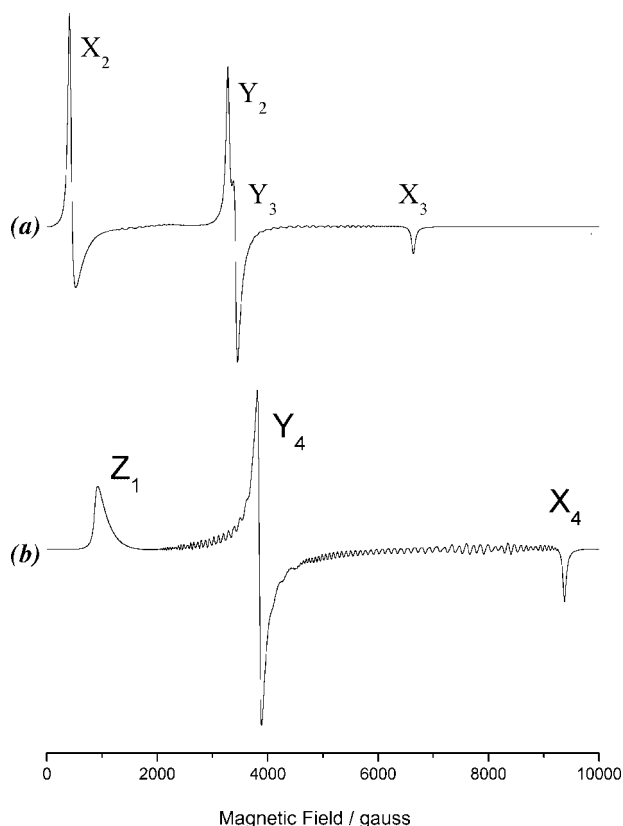
Figure 4. Simulated ESR transitions ($\nu_0 = 9.562$ GHz) for a randomly oriented quintet spin-state with $g = 2.0023$, $|D/hc| = 0.191$ cm^{-1} and $|E/hc| = 0.0625$ cm^{-1}, showing: (a) $W_{\pm 1}/W_0$ transitions; (b) $W_{\pm 2}/W_{\pm 1}$ transitions. Note that Z_1 overlaps X_1, Y_4 overlaps Y_1, and X_4 overlaps Z_4 transitions

corresponding quintet dinitrenes from the SIM ESR simulations can be well-rationalized by appropriate choice of the geometric parameter $\alpha = (\theta/2)$. Using $\theta = 114°$ and $|D_t/hc| = 1.029$ cm^{-1} for **6a** then $D_q/hc = 0.191$ cm^{-1} and $E_q/hc = (-)0.0514$ cm^{-1}; using $\theta = 116°$ and $|D_t/hc| = 1.068$ cm^{-1} for **6b** then $D_q/hc = 0.206$ cm^{-1} and $E_q/hc = (-)0.0506$ cm^{-1}. UB3LYP/6-31G* calculations for quintet dinitrenes **6a,b** were carried out using the Gaussian program.[21] They support the argument that the zfs parameters are explained by θ being several degrees smaller than 120°; the vector angles θ in quintet dinitrenes **6a,b** are computed to be 114.7° and 114.5°, respectively. The computations and experimental zfs assignments both imply a smaller vector angle θ in quintets **6a,b** than the nominal *meta*-connectivity angle of 120°. The computed θ are also somewhat smaller for **6a,b** than the 117° angles computed[14] for 2,6-dinitrenopyridine itself at the same level of theory, showing how substituent effects can influence both θ and the overall zfs. The UB3LYP/6-31G* calculations also showed that nitrenes **5a**, **5b**, **6a**, and **6b** have Mulliken spin populations on their nitrene nitrogens of 1.596, 1.608, 1.644, and 1.658, respectively. The higher spin populations on the nitrenes of **5b** and **6b** by comparison with

5a and **6a** should give somewhat larger D-values in the former species; this is the experimentally observed trend.

It is not necessary to presume major *electronic* perturbation of the individual nitrene units in these 2,6-dinitrenopyridines due to heteroatom spin polarization effects, which was earlier suggested[14] as one possible cause of the unusual ESR line positions by comparison to *meta*-phenylenedinitrenes. If the unusual line positions in 2,6-dinitrenopyridines indicated unusually large zfs D-values,[14] this would not agree well with dipolar model estimates. This present study provides more precise zfs estimation with lineshape simulations, and shows a reasonable agreement of experimental quintet state zfs with expectations of dipolar interaction between mononitrene sites. The primary cause of the ESR peak shifts relative to **3** thus seems to be *geometric* perturbation of the nominally 120° *meta* zfs tensor interaction vector angle between the mononitrene units, due to the linkage of the nitrene units by a heterocyclic pyridine ring instead of a phenylene ring, and to effects of exocyclic substituents.

CONCLUSION

The zfs and computational analyses of two typical 2,6-dinitrenopyridine X-band ESR spectra support the dipolar model for interpreting quintet zfs based upon the vector angle formed between interacting triplet mononitrene units. The unusual quintet zfs by comparison to structurally related *meta*-phenylenedinitrenes are most reasonably attributed to geometric perturbation away from the ideal 120° *meta* vector angle, due to electronic effects of the pyridine ring and attached exocyclic substituents. It is not necessary to suppose major spin density perturbations in the component mononitrene units to explain the zfs trends. This is an important verification of the applicability of the dipolar model of zfs for a system that is subject to heteroatom perturbation of π-spin density, especially with regard to possible increases in the effects of inter-nitrene zfs tensor interaction (these are typically[18b] assumed to be much smaller than one-center mononitrene zfs terms in application of the model).

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Selected geometrical parameters of triplet nitrenes 5a,b and quintet dinitrenes 6a,b calculated using UB3LYP/6-31G*.
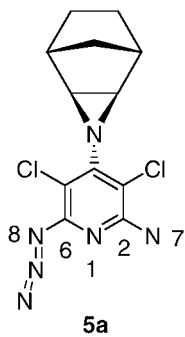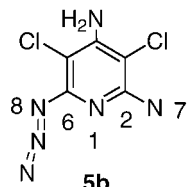

Bond lengths:
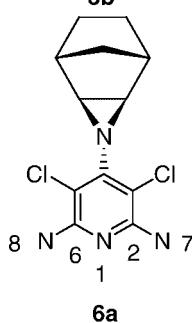C(2) - N(7) = 1.333 A
C(6) - N(8) = 1.406 A
N(1) - C(2) = 1.368 A
N(1) - C(6) = 1.316 A

Bond angles:
$\phi' = N(1) - C(2) - N(7) = 117.3^0$
$\phi'' = N(1) - C(6) - N(8) = 119.5^0$
$\omega = C(2) - N(1) - C(6) = 118.0^0$

Energy = -1711.9849655 hartrees; $<S^2> = 2.048$

5a

Bond lengths:
C(2) - N(7) = 1.335 A
C(6) - N(8) = 1.405 A
N(1) - C(2) = 1.369 A
N(1) - C(6) = 1.318 A

Bond angles:
$\phi' = N(1) - C(2) - N(7) = 117.4^0$
$\phi'' = N(1) - C(6) - N(8) = 119.7^0$
$\omega = C(2) - N(1) - C(6) = 118.0^0$
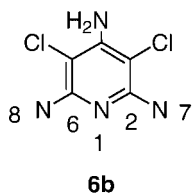
Energy = -1440.47813 hartrees; $<S^2> = 2.045$

5b

Bond lengths:
C(2) - N(7) = 1.341 A
C(6) - N(8) = 1.341 A
N(1) - C(2) = 1.365 A
N(1) - C(6) = 1.365 A

Bond angles:
$\phi' = N(1) - C(2) - N(7) = 116.0^0$
$\phi'' = N(1) - C(6) - N(8) = 116.0^0$
$\omega = C(2) - N(1) - C(6) = 117.3^0$

Energy = -1602.4436486 hartrees; $<S^2> = 6.096$

6a

Bond lengths:
C(2) - N(7) = 1.342 A
C(6) - N(8) = 1.342 A
N(1) - C(2) = 1.357 A
N(1) - C(6) = 1.357 A

Bond angles:
$\phi' = N(1) - C(2) - N(7) = 116.0^0$
$\phi'' = N(1) - C(6) - N(8) = 116.0^0$
$\omega = C(2) - N(1) - C(6) = 117.5^0$

Energy = -1330.9360847 hartrees; $<S^2> = 6.092$

6b

$$\theta = 120 - (120 - \phi') - (120 - \phi'') + (120 - \omega) = \phi' + \phi'' - \omega$$