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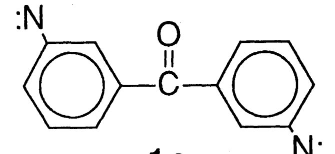
ESR of Excited Quintet States in 3,3'-Dinitrenobenzophenone

Shigeaki NIMURA, Osamu KIKUCHI, Tsuguyori OHANA,† Akira YABE,† and Masahiro KAISE†*
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305
†National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305

Two excited quintet states of 3,3'-dinitrenobenzophenone were observed by ESR in frozen organic matrix. One of their zero field splitting parameters were estimated to be $D = 0.168\ \mathrm{cm^{-1}}$ and $E = 0.024\ \mathrm{cm^{-1}}$.

Recently, the research on organic ferromagnets is an area of increasing interest.[1-5] Several groups have studied the intramolecular magnetic interaction of open-shell units.[2-5] In the course of our investigation of nitrenes,[6] we studied the intramolecular magnetic interactions of two nitreno groups in 3,3'- and 4,4'-dinitrenobenzophenone (**1a**, **2a**). Shortly before submitting a manuscript of our experimental results, a similar study was reported by Lahti's group.[3] In the case of **1a**, however, some novel results were obtained for the magnetic interactions of two nitreno groups, though we obtained similar results in the ESR study of **2a**. In this paper, we report the zfs parameters and conformational analysis of **1a**.



1a

3,3'-Diazidobenzophenone (**1b**), the precursor of **1a**, was synthesized by diazotization of the corresponding diamine and following addition of sodium azide. The diazide was dissolved in 2-methyltetrahydrofuran and the solution was degassed by freeze-thaw cycles. The dinitrene was generated upon the irradiation of the dilute frozen solution (ca. 10^{-3} mol $\mathrm{dm^{-3}}$) with a filtered high-pressure mercury lamp ($270\ \mathrm{nm} < \lambda < 400\ \mathrm{nm}$). The ESR spectra were taken on an ESR spectrometer (JEOL JES - RE3X) equipped with a liquid helium transfer system (Air Products Model LTR-3).

Figure 1 shows the ESR spectrum obtained by the photolysis of **1b** at 70 K. Resonances at 680 and 322 mT are respectively assigned to the transitions of a triplet mononitrene and doublet radicals. We also observed signals at 10 - 100 (broad), 235, 295, and 860 (weak) mT. The peak at 860 mT is due to a typical quintet dinitrene which has not been observed by Lahti's group. This new finding would be attributable to the optimum conditions of the sample solution and the light source. The temperature dependence of signals at 10 - 100, 235, 295, and 860 mT was carefully studied in the range 4 - 50 K. The intensities of the peaks at 10 - 100, 295, and 860 mT reached a maximum at approximately 10 K (Fig. 2). The similarity of the spectrum to the quintet dinitrene spectra appeared in the literature[3-5] suggests that the signals at 10 - 100, 295, and 860 mT are assigned to the thermally excited quintet state of **1a** ascribed to conformational isomer(s) as shown in Fig. 3. If we assume that the highest field transition is the resonance at 860 mT and the next highest is hidden under the intense mononitrene resonance at 680 mT, the zfs parameters of **1a** are estimated to be $D = 0.168\ \mathrm{cm^{-1}}$ and $E = 0.024\ \mathrm{cm^{-1}}$ on the basis of a third-order perturbation theory with a high-field approximation.[7] The peak at 235 mT reached a maximum at about 20 K (Fig. 2). The irreversible thermal decay rates of the signals at 235 and

295 mT were investigated to determine the origin of the 235 mT resonance. Their decay rates were different from each other, indicating that the two signals originated from two species. Hence it is reasonable to conclude that the signal at 235 mT originates from another conformer(s) of **1a** in a thermally excited quintet state. Sasaki and Iwamura[5)] also observed two sets of quintet resonances due to two conformers. The corresponding characteristic resonance of the quintet dinitrene expected at about 850 mT could not be observed in our study, probably because it was too weak to detect or hidden under the 860 mT resonance. We estimated two energy gaps between the singlet ground state and the excited quintet state on the basis of Curie law analysis of ESR signal intensity as a function of temperature according to the same method used by Lahti's group.[3)] One is 28 cal /mol for the quintet signals at 10 - 100, 295, and 860 mT. The other is 60 cal /mol for the quintet signal at 235 mT. Figure 2 shows the Curie plots and the fitted curves for the resonances at 235 and 295 mT. In conclusion, we observed two different quintet states of **1a**, the energy gaps between the singlet and the quintet state and one of their zfs parameters were estimated, while Lahti's group has not assigned the signals at 235 and 295 mT to different species and they have not estimated the zfs parameters of **1a**.[3)]

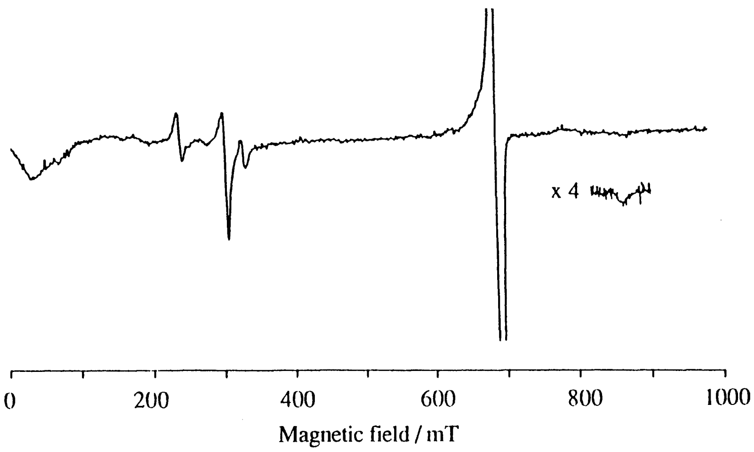


Fig. 1. ESR spectrum obtained after irradiation of **1b** at 70 K (ν = 9.1148 G Hz).

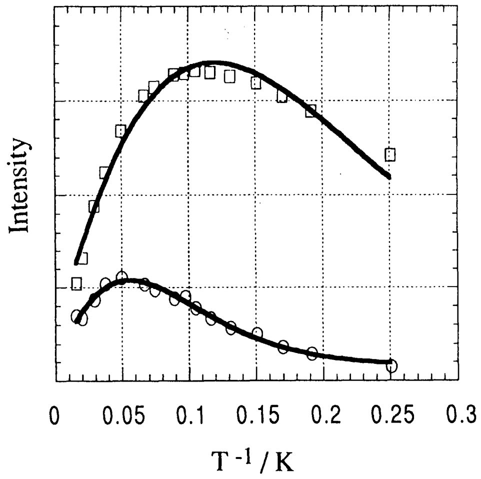


Fig. 2. Curie plots and the fitted curves for the signals at 235 (○) and 295 (□) mT.

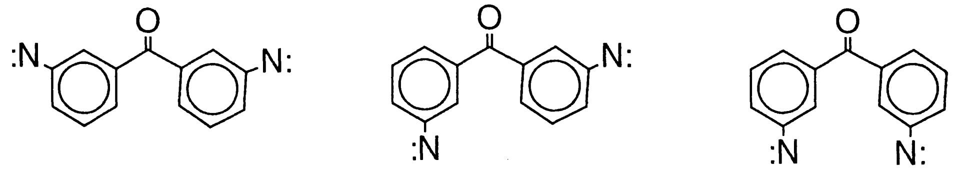


Fig. 3. Three conformational isomers for **1a**.

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