Singlet-Triplet Energy Gaps of Quinonoidal Dinitrenes

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

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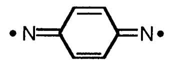
Singlet-triplet energy gaps of phenylene-1,4-dinitrene (**1**), biphenyl-4,4'-dinitrene (**2**), stilbene-4,4'-dinitrene (**3**), and azobenzene-4,4'-dinitrene (**4**) were determined from temperature dependence of ESR signal intensities. These quinonoidal dinitrenes show interesting features: (1) the energy gap of **1** is comparable to that of **2**, and (2) the gap of **4** is almost one-half of the gap of **3**. The results are qualitatively explained by magnitudes of polarized π spins.

The magnetic intramolecular interactions in dinitrenes have become much investigated in connection with organic high-spin molecules and reactive intermediates.[1-11] Quinonoidal dinitrenes phenylene-1,4-dinitrene (**1**), biphenyl-4,4'-dinitrene (**2**), stilbene-4,4'-dinitrene (**3**), and azobenzene-4,4'-dinitrene (**4**) have been also investigated by several groups,[4-9] and they have interesting features as follows. First, the experimental zero-field splitting D values were very large compared to the D values which are estimated theoretically by a point-dipole approximation. Second, although the inter-electronic distance is longer in **2** than **1**, the D value of **2** is larger than that of **1**. Third, the inter-electronic distance is similar in **3** and **4**, though the D value of **3** is larger than that of **4**. In addition, it has been reported that the ground-state of **4** is triplet[5] in disagreement with the valence bond consideration while those of **1**, **2**, and **3** are singlet.[8,9] To understand those properties and ground-state multiplicities, we investigated the singlet-triplet energy gaps in **1**, **2**, **3**, and **4**.



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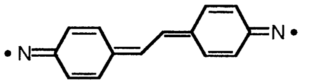

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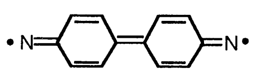

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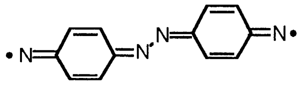

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The diazide precursors of the molecules **1**, **2**, **3**, and **4** were dissolved in 2-methyltetrahydrofuran. These dilute frozen solutions (ca. 10^{-3} mol dm^{-3}), which were degassed by freeze-pump-thaw cycles, were irradiated with a xenon lamp through a filter (270 nm < λ < 400 nm) to generate the dinitrenes. The ESR spectra were taken on an X-band ESR spectrometer (JEOL JES-RE3X) equipped with a liquid helium transfer system (Air Products Model LTR-3) in the range of 30 to 80 K. The measurements were carried out at an appropriate low microwave power for each dinitrene triplet signal to avoid the signal saturation effect. The sample temperatures were monitored continuously just below the ESR cavity. In addition, the temperatures were calibrated by measuring temperatures at the actual position with a chromel-AuFe thermocouple placed in a sample tube before each ESR experiment.

We obtained triplet ESR signals of quinonoidal dinitrenes (**1**-**4**) in photolyses of diazide precursors. The D values (Table 1) determined from these signals are in fair agreement with those previous reported.[4-9] Moreover, the temperature dependence of these triplet signal intensities was measured three times independently for each dinitrene as shown in Figure 1. All plots indicate that those quinonoidal dinitrenes have singlet ground states including dinitrene **4**.[5] Thus the ground state of **4** is also in agreement with the valence bond consideration. To determine the singlet-triplet energy gaps of quinonoidal dinitrenes, these plots were fitted by

$$I = \frac{C}{T}\frac{3\exp(-E/RT)}{1+3\exp(-E/RT)}$$

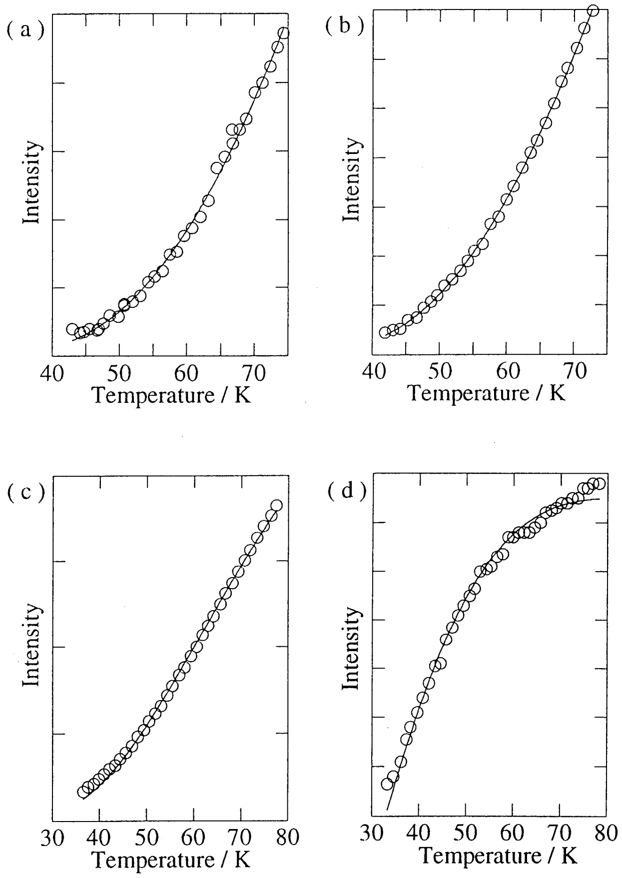


Figure 1. ESR signal intensities vs. temperature of **1** (a), **2** (b), **3** (c), and **4** (d) with fitted curves. One of the three plots is shown for each compound.

Table 1. Singlet-triplet energy gaps and D values of quinonoidal dinitrenes

Compound	S-T gap[a] / kcal mol^{-1}	D value / cm^{-1}
1	0.722 ± 0.007	0.169
2	0.750 ± 0.017	0.191
3	0.472 ± 0.008	0.123
4	0.251 ± 0.002	0.058

[a] The values are average data from three plots.

where I is the intensity, C is a constant, E is the singlet-triplet energy gap, R is the gas constant, and T is the absolute temperature. Table 1 lists those singlet-triplet energy gaps in **1**-**4**.[6]

In the above results, there are two points we should emphasize: (1) the gap of **1** is comparable to that of **2**, though those spins interact through completely different π systems, and (2) the energy gap of **4** is almost one-half of the gap of **3**, while their π systems are similar. These interesting findings are discussed in terms of interactions of localized σ spins through π systems.

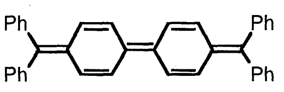
The interaction between localized σ spins can be divided into two parts. One is spin polarization of π spin on nitrene nitrogen by the localized σ spin. The other is interaction between these polarized π spins. The localized σ spins are closer in **1** than **2**. Thus if the magnitudes of polarized π spin in **1** and **2** were the same, the interaction between these spins would be stronger in **1** than **2**. The similarity of the gaps implies that the magnitude of polarized π spin in **1** is smaller than that in **2**. That is to say, the two factors, the magnitude of polarized π spin and the interaction between the terminal π spins, cancel out and result in the similar gaps in **1** and **2**.

Now let us consider a dinitrene character in **1** and **2**, which has two unpaired electrons on each nitrene nitrogen. The dinitrene character can relate to the magnitude of polarized π spin. Thus the results discussed above also suggest that the dinitrene character is smaller in **1** than **2**. This is also consistent with following observations.

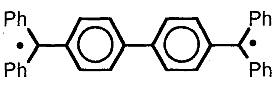
We previously reported the specific C=N stretching bands in **1** at 1759 and 1775 cm^{-1},[10] while we have observed no such bands in **2**.[11] Moreover, Chichibabin's hydrocarbon, which is analogous with **2** in terms of the π system, has shown triplet ESR signals[12] and has an unusual large diradical character.[13] These results indicate that the contribution of the dinitrene character is small in **1** while that is relatively large in **2**.

In addition, we suppose that the large D values of **1** and **2** are mainly due to the induced π spins on nitrogens from analogy to similar dicarbenes.[14] Then, the smaller magnitude of polarized π spin in **1** than **2** is also in agreement with that the D value of **1** is smaller than that of **2**.

dinitrene structures for **1** and **2**



Chichibabin's hydrocarbon



diradical structure

In a similar manner, the π systems of **3** and **4** are similar, thus the difference of singlet-triplet energy gap may result mainly from the smaller magnitude of polarized π spin in **4** than **3**.[15] This is also consistent with that the D value of **4** is one-half of that of **3**.

Further studies of relationships between singlet-triplet energy gaps and D values for some other quinonoidal dinitrenes are now in progress.

References and Notes

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15. A decrease of conjugation due to twist of the π system is one possibility for the reducing energy gap. Nevertheless, we observed mononitrene ESR signals of 4-azido-4'-nitreno-stilbene (**A**) and 4-azido-4'-nitreno-azobenzene (**B**), and these D vales are 0.773 cm^{-1} and 0.748 cm^{-1}, respectively. The results indicate that π spin is well delocalized in **B** compare to **A**. Thus the decrease of conjugation could be excluded as the reason for the reducing gap.