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2,2'-Dimethylbiphenyl-4,4'-dinitrene

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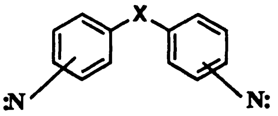
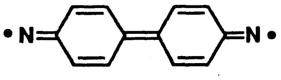
Photolysis of 2,2'-dimethylbiphenyl-4,4'-diazide in a glassy matrix at 77 K gives first a mononitrene ESR peak ($|D/hc| = 0.95$ cm^{-1}), followed by production of a lower field peak attributable to a twisted biphenyl-4,4'-dinitrene ($|D/hc| = 0.93$ cm^{-1}), in which two nitrene moieties are electronically isolated from one another by torsion.

As part of our research involved in the design of new magnetic materials, our group has embarked on the study of high-spin bis(arylnitrene)s (general structure **1**) in an effort to understand the relationship between molecular connectivity/geometry and ground state spin multiplicity,1-2) a crucial component of design strategies aimed at devising new bulk ferromagnets. Different qualitative molecular connectivity rules normally are used with an assumption of near-planar molecular geometries,3-5) in order to predict ground state spin multiplicities of pi-conjugated open-shell molecules. The effect of torsional deconjugation in breaking pi-connectivity is therefore important1a) for such systems. We have studied various torsionally uninhibited biphenyldinitrenes in other work.1b-d) Both our group6) and that of Yabe7) have found that biphenyl-4,4'-dinitrene, **2**, in a planar or near-planar geometry is a quinonoidal singlet biradical with a thermally accessible triplet state. The Yabe group7) in addition has found evidence for a bisected geometry of **2** under certain experimental conditions. In this contribution, we report the generation of 2,2'-dimethyl-biphenyl-4,4'-dinitrene, **3**, a system which cannot achieve a near-planar geometry, and which must therefore be conformationally deconjugated (non-quinonoidal). Our results appear to support the Yabe group's contention for existence of a bisected form of **2**.

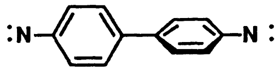
Bis(arylnitrene) **3** was generated by photolysis of the corresponding diazide **4**8) through monochromator (320 nm) with a 1000 W xenon arc lamp in glassy 2-methyl-



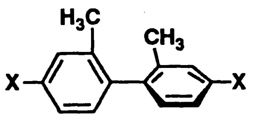
1



2
(planar)



2
(bisected)



3 **X = N:**
4 **X = N$_3$**

tetrahydrofuran at 77 K. The X-band electron spin resonance (ESR) spectrum obtained under these conditions is shown in Fig. 1. The dominant features of the ESR spectrum are peaks at 3350 G, 6750 G, and 6820 G. The peak at ca. 3350 G varies with irradiation conditions, and is due to radical impurities that are often observed in irradiation of aryl nitrenes. The 6820 G peak corresponds to photolysis of a single azide moiety in **4** to give a mononitrene, and is formed within 15 s of photolysis. This mononitrene peak position ($|D/hc|$ = 0.95 cm^{-1}) shows a lack of conjugation, as expected by comparison to the substantially lower field resonance (6480 G, $|D/hc|$ = 0.83 cm^{-1}) of the mononitrene derived from photolysis of biphenyl-4,4'-diazide.[6] The peak at 6750 G grows in subsequently to the mononitrene peak, and partly overlays it as photolysis of **4** is continued. It is very similar in position and lineshape to an ESR peak assigned by Yabe and coworkers[7] to a twisted isomer of **2** generated under analogous conditions. This peak we assign to **3**. Long-term (> 5 min) photolysis through Pyrex led to bleaching of the mononitrene peak and the peak assigned to **3**, with concurrent growth of the radical peak at

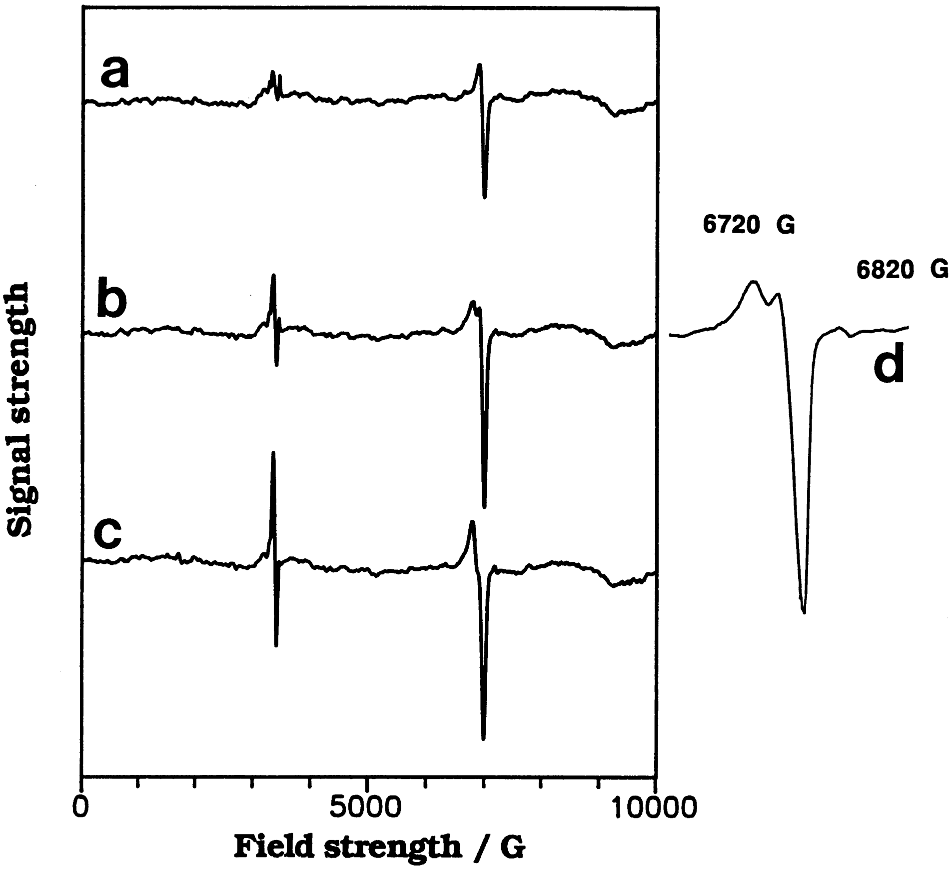


Fig. 1. ESR 9.57 GHz spectra from irradiation of **4** in glassy 2-methyltetrahydrofuran at 77 K and 320 nm for 45 s (a), 945 s (b), and 2505 s (c); (d) is a blowup of the nitrene region of spectrum (b).

3350 G, as well as peaks from other, still-unidentified species: milder photolysis using monochromator-filtered light at 320 nm avoided this bleaching problem.

Brief photolysis of **4** thus leads initially to a mononitrene, and sequentially next to bisected dinitrene **3**. The ESR spectrum of **3** is consistent with that expected of a pair of essentially isolated mononitrenes with $|D/hc| = 0.93$ cm^{-1}, judging by the presence of the single peak with its magnetic resonant field position in the mononitrene region. Also, photolysis of **4** at 320 nm in 2-methyltetrahydrofuran at 77 K leads to complete depletion of the azide UV-VIS absorption maximum at 268 nm and concomitant growth of a new peak at 432 nm (plus a very weak shoulder at 550 nm). No other major UV-VIS absorptions are produced upon extended photolysis at 320 nm (Fig. 2). Since the ESR spectrum shows sequential photolysis of azide units, the UV-VIS spectrum of **3** apparently overlays that of mononitrene from **4**, further implying structural similarity.

Semiempirical molecular orbital computations (AM1-CI method[1]) show virtually no interaction of nitrene sites in bisected **2**, while the planar form of **2** is computed to be have a ^1A_g diradical ground state with a localized n,π* ($^3B_{1u}$) triplet state 1920-3760 J/mol higher in energy (the experimental[6] $S \rightarrow T$ gap for planar **2** in 2-methyltetrahydrofuran is 2440 J/mol). It is difficult to compare reliably semiempirical results for two species so different as planar and bisected **2**, but AM1-CI suggests that the two forms are within about 20 kJ/mol in energy. Benzenoid delocalization in the twisted form can compensate for loss of quinonoid bonding in

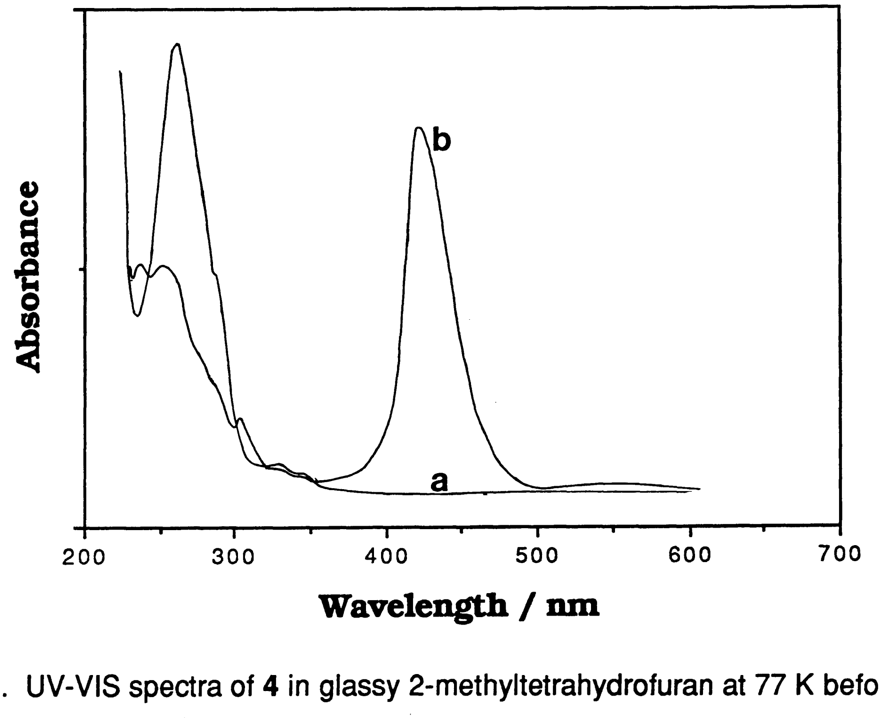


Fig. 2. UV-VIS spectra of **4** in glassy 2-methyltetrahydrofuran at 77 K before (a) and after (b) irradiation at 320 nm.

going from the planar to the bisected form of **2**. One might have predicted based upon pi-spin polarization arguments that bisected **2** and **3** could exhibit quintet state electronic properties, since the 1 and 1' positions in the bisected biphenyl ring should have parallel spins (same sign of spin density). But, our semiempirical computations showed only a very small magnitude of interaction between spins in the bisected geometry of **2**, hence the two nitrene centers are electronically nearly isolated, as indicated by the mononitrene-like ESR spectra.

These results exemplify the fact that conformational deconjugation caused either by structural, morphological, or chemical/photochemical influences can have a substantial effect on the electronic nature of open-shell molecules, and that such conformational effects should be considered in design strategies aimed at synthesis of very high spin organic systems with potentially interesting magnetic properties.

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8) 2,2'-Dimethylbiphenyl-4,4'-diazide: light tan solid with mp 33-34 °C. IR (KBr, cm^{-1}): 2110 (strong, N=N=N str). UV-VIS (THF, λ_{max}/nm, ε_{max}): 262 (29 910). Analysis: Found: C 63.34%, H 4.62%, N 31.64%. Calculated for $C_{14}H_{12}N_6$: C 63.63%, H 4.58%, N 31.79%.

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