An Exceptionally Simple Method of Preparation of Biradicals. 2. Low-Temperature Fluorescence Spectra and Ambient Temperature Laser-Induced Fluorescence Spectra of 1,3-, 1,6-, 2,6-, and 2,7-Naphthoquinodimethane[1]

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Abstract: 1,3-, 1,6-, 2,6-, and 2,7-naphthoquinodimethane have been obtained by photolysis (254 nm) of bis(chloromethyl)naphthalenes in glassy media at 77 K or in solution at ambient temperature by KrF (249 nm) laser flash photolysis. These species are detected and characterized by fluorescence spectroscopy.

Introduction

The preparation and spectroscopy of non-Kekulé hydrocarbons continues to be of interest. Several members of this class of compounds are known, including trimethylenemethane (1),[2] tetramethyleneethane (2),[3] 1,8-naphthoquinodimethane (3),[4] and 2,4-dimethylene-1,3-cyclobutanediyl (4).[5] Simple MO and PMO
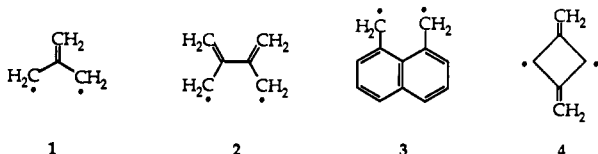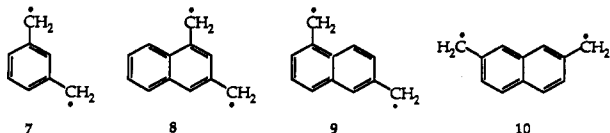

theories predict that biradicals 1–4 have a pair of degenerate, nonbonding molecular orbitals in which to accommodate two electrons.[4a] Thus, by extension of Hund's first rule to molecules, compounds 1–4 are predicted to have ground triplet states.[4a,6] The predictions of simple theoretical methods are consistent with experiments with biradicals 1–4.

Biradicals such as 1–4 have usually been prepared from precursors in which proximal terminii of the biradicals have been linked by a small group such as molecular nitrogen or carbon monoxide which can be extruded upon photolysis (e.g., 5 → 6).[2–5]
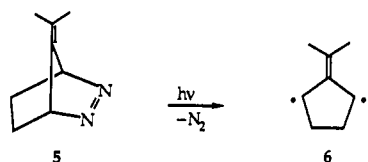

The decomposition of a cyclic precursor is rather awkward for *m*-xylylene (7) and 1,3-naphthoquinodimethane (8), and appears to be an even less promising strategy for preparing 1,6- and 2,7-naphthoquinodimethane (9 and 10, respectively). Accord-


ingly, *m*-xylylene (7) has been prepared by several alternative routes that do not require a cyclic precursor.[1,7] Recently we have reported that 7 can be formed cleanly by 254-nm photolysis of dichloride 12a immobilized in glassy ethanol at 77 K and subsequently detected by fluorescence spectroscopy[1] and that the laser-induced fluorescence spectrum of 7 can be obtained by KrF excimer laser photolysis of dibromide 12b in solution at ambient

temperature.[8] Herein we are pleased to report that this methodology can be extended to the previously unknown biradicals 8–10.
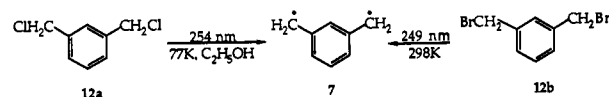
Simple Hückel MO and PMO theories predict that 8–10 contain a pair of degenerate nonbonding molecular orbitals, and as a consequence they should all be ground-state triplet biradicals as per *m*-xylylene.[4a,6] Alternatively, in 2,6-naphthoquinodimethane (11) a degenerate pair of NBMOs is no longer present, the
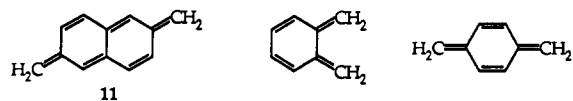
HOMO and LUMO levels are split, and the molecule is predicted to be a singlet-state biradicaloid as per 1,2- and 1,4-benzo-quinodimethane (*o*- and *p*-xylylene, respectively).[4a,6] Analysis of

(1) For part 1 of this series see: Haider, K.; Platz, M. S.; Després, A; Lejeune, V.; Migirdicyan, E.; Bally, T.; Haselbach, E. *J. Am. Chem. Soc.* **1988**, *110*, 2318.

(2) (a) Dowd, P. *J. Am. Chem. Soc.* **1966**, *88*, 2587. (b) Berson, J. A. *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; p 151.

(3) (a) Dowd, P. *J. Am. Chem. Soc.* **1970**, *92*, 1066. (b) Dowd, P. Chang, W.; Paik, Y. H. *J. Am. Chem. Soc.* **1986**, *108*, 7416. (c) Dowd, P.; Chang, W.; Paik, Y. H. *J. Am. Chem. Soc.* **1987**, *109*, 5284.

(4) (a) Platz, M. S. *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982. (b) Watson, C. R., Jr.; Pagni, R. M.; Dodd, J. R.; Bloor, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 2551. (c) Pagni, R. M.; Burnett, M. N.; Dodd, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 1972. (d) Pagni, R. M.; Watson, C. R., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 2291. (e) Pagni, R. M.; Watson, C. R., Jr.; Bloor, J. E.; Dodd, J. R. *J. Am. Chem. Soc.* **1974**, *96*, 4064. (f) Muller, J. F.; Muller, D.; Dewey, H.; Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 1627. (g) Gisin, M.; Rommel, E.; Wirz, J.; Burnett, M. N.; Pagni, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 2216.

(5) (a) Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 1774. (b) Dowd, P.; Paik, Y. H. *J. Am. Chem. Soc.* (c) Dougherty, D. A. *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, 1990; p 117.

(6) (a) Hund, F. *Linienspektren und periodisches System der Elemente*; Springer-Verlag: Berlin, 1927, p 124. (b) Coulson, C. A.; Streitwieser, A. *Dictionary of π Electron Calculations*; Freeman: San Francisco, 1965. (c) Borden, W. T. *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; p 1. (d) Davidson, E. R. *Ibid.*; p 73.

(7) (a) Migirdicyan, E. *Hebd. Seances Acad. Sci.* **1968**, *266*, 756. (b) Migirdicyan, E.; Baudet, J. *J. Am. Chem. Soc.* **1975**, *97*, 7400. (c) Wright, B. B.; Platz, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 628. (d) Goodman, J. L.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 5409.

(8) Haider, K.; Migirdicyan, E.; Soundararajan, N.; Platz, M. S.; Després, A. *J. Am. Chem. Soc.* **1990**, *112*, 733.

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Table I. Details of the Fluorescence Spectra of Naphthoquinodimethane Biradicals and Naphthylmethyl Radicals at 77 K

λ_{exc}, nm	radical or biradical	fluorescence maxima, nm	theory,[d,12] nm	spacing, cm⁻¹
363	1,3-NQM[a] (8)	525,[d] 542, 567.5	539	560, 1390
350	1,6-NQM[b] (9)	545,[d] 560, 589	542	490, 1375
348	2,7-NQM[a] (10)	561.5,[d] 575, 609	511	435, 1405
	1,8-NQM[a] (18)[c]	512[d]	509	
369	2,6-NQM[a] (11)	435,[d] 462.5, 493		1370, 2705
	1-NpCH₂[•e]	586,[d] 607, 644[e]		599, 1537[e]
	1-NpCH₂[•f]	586.5,[d] 604, 638[f]		494, 1376[f]
	2-NpCH₂[•e]	595,[d] 612, 650		470, 1422
295	1,3-BQM (7)	440,[d] 470		
295	1,2-BQM (19)	414[d]		

[a] 2-MTHF. [b] Ethanol. [c] An ethano-bridged 1,8-NQM in EPA; see ref 5g. [d] Zero–zero band. [e] Solution phase, ref 10. [f] This work; rigid glass.

the fluorescence spectra of **8–11** will be found to be consistent with the predictions of simple theories and that **8–10** are indeed triplet biradicals whereas **11** is most likely a singlet-state biradicaloid.[9]

Results and Discussion

Triplet Biradicals 8–10. Dichlorides **13a–15a** and dibromides **13b–15b** were easily prepared by dibromination of the appropriate dimethylnaphthalene or by stirring the appropriate diols with either aqueous HCl or HBr.

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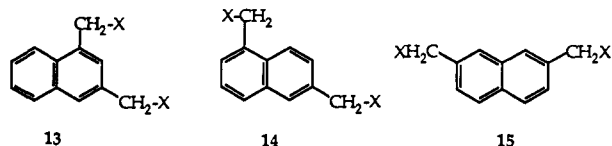
X = (a) Cl (b) Br

Brief photolysis of dilute solid–solid solutions of 1,3-, 1,6-, and 2,7-bis(chloromethyl)naphthalene **13a–15a** in ethanol-d_6 or 2-methyltetrahydrofuran (2-MTHF) at 77 K, followed by excitation between 348 and 369 nm, produces the emission spectra presented in Figure 1a–c. The fluorescence spectra of Figure 1a–c are not observed prior to 254-nm photolysis of dichlorides **13a–15a**. The spectra disappear when the sample is warmed to room temperature and then cooled again to 77 K. Fluorescence attributable to the 1- or 2-naphthylmethyl radical, or of their simple alkyl derivatives, is expected between 595 and 605 nm and either is not present or is of low intensity (Table 1).[10]

The prolonged photolysis of naphthalene in ethanol at 77 K ultimately leads to the formation of a new species with a broad emission starting at 540 nm. This emission has been attributed to radical **16** since it is located in the same spectral region and resembles the envelope of the well-resolved low-temperature fluorescence spectrum of this radical produced by ionizing radiation in naphthalene crystals.[11] In our experiments, radical **16** is probably produced as a result of excitation of triplet naphthalene to a very highly excited triplet state.[11] The very highly excited triplet state can abstract a hydrogen atom from the host medium to produce a benzocyclohexadienyl type of radical. Fluorescence attributable to a hydronaphthyl derivative of **13–15** (e.g., **17**) expected at 540 nm is barely discernible in the spectra

16 17
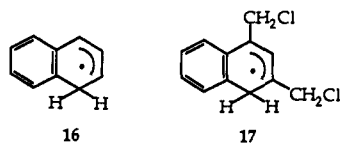
of **8** and **9** (Figure 1a,b) produced by brief (60 s, 254 nm) photolysis of the precursor and excited at the specific excitation

(9) Flynn, C. R.; Michl, J. *J. Am. Chem. Soc.* **1974**, *96*, 3280.

(10) (a) Hilinski, E.; Huppert, D.; Kelley, D. F.; Milton, S. V.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 1951. (b) Kelley, D. F.; Milton, S. V.; Huppert, D.; Rentzepis, P. M. *J. Phys. Chem.* **1983**, *87*, 1842. (c) Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6368. (d) Tokumura, K.; Udagawa, M.; Itoh, M. *J. Phys. Chem.* **1985**, *89*, 5147.

(11) Jacobsen, C. W.; Hong. H.-K.; Sheng, S. J. *J. Phys. Chem.* **1978**, *82*, 1357.
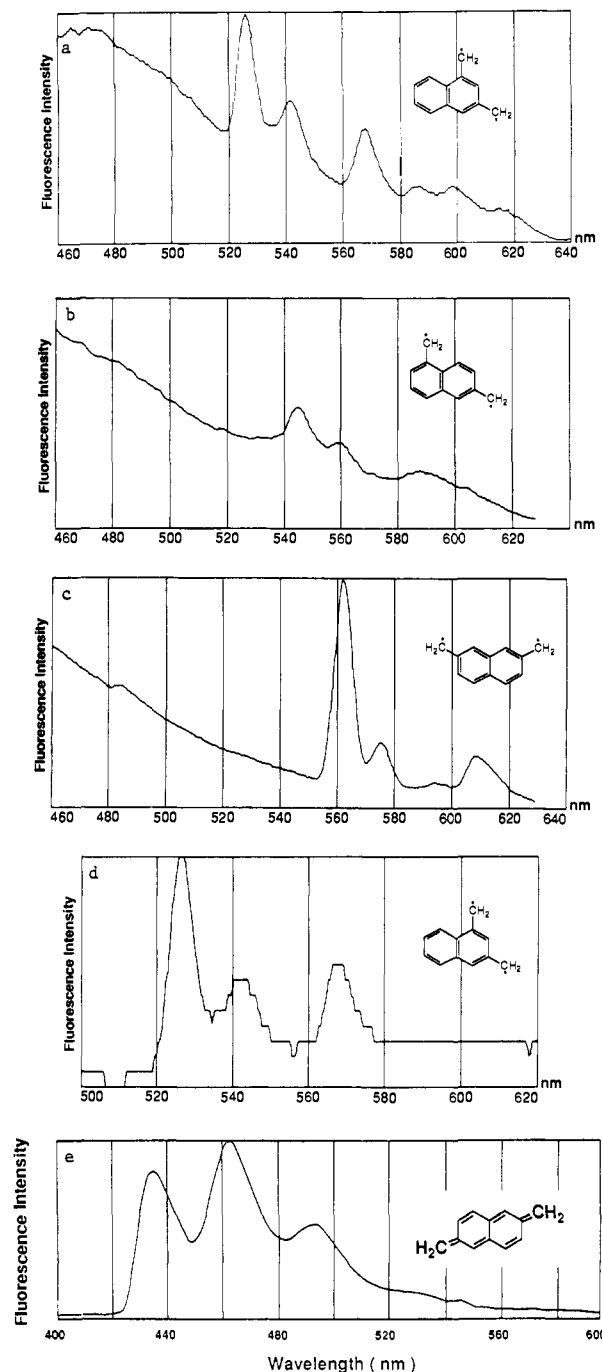
Figure 1. Fluorescence spectra of biradicals (a) **8**, (b) **9**, and (c) **10**, produced by photolysis (254 nm) of dichloride precursors **13a–15a** at 77 K, of (d) **8**, produced by electron bombardment of the precursor at 77 K, and of (e) biradicaloid **11** (see Table 1).

wavelength listed in Table 1. The emission spectrum produced from dichloride **15a** is particularly intense (Figure 1c) and is not

contaminated with the emission of a hydronaphthyl type of radical. The emission bands depicted in Figure 1a–c are attributed to 1,3-, 1,6-, and 2,7-naphthoquinodimethane (NQM) because they are in the same spectral region as the fluorescence of the ethano-bridged 1,8-NQM derivative[4g] 18 and in the region predicted for 1,3-, 1,6-, and 2,7-NQM by Gisin and Wirz (Table I).[12]
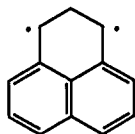
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In further support of this assignment we note that a weak fluorescence spectrum of 8 at 77 K was found (Figure 1d) that is identical with the spectrum of Figure 1a, after exposure of 1,3-bis(chloromethyl)naphthalene (in glassy 2-methyltetra-hydrofuran) to 3.5-MeV electrons produced from a linear accelerator. The biradical is presumably formed by double-disso-ciative electron capture under these conditions.[1]
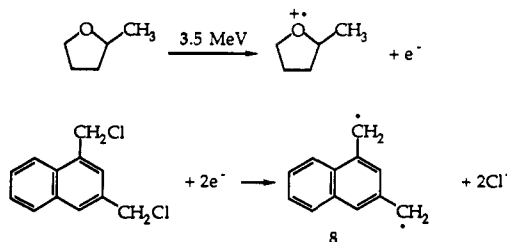
The fluorescence spectrum of each NQM triplet biradical presents a zero–zero band and two vibrational bands. The excitation spectra 1–111 of the three fluorescence bands of a given NQM are very similar, consistent with mainly a single carrier of the fluorescence spectrum (Figure 2a–c). Hydronaphthyl radical derivatives of 13 (e.g., 17) and of precursor 14 contribute slightly to excitation bands of 8 and 9 near 340 nm (Figure 2a,b).

The frequencies of the vibrational bands observed in the fluorescence spectra of naphthoquinodimethanes 8–10 are listed in Table I. They are very close to the ground-state frequencies of 510 and 1380 cm^{-1} of the naphthalene molecule.[13]

The observations mirror the results obtained with *m*-xylylene (7) and its methylated derivatives, the fluorescence spectra of which were analyzed by using the modes and ground-state frequencies of the corresponding methylated benzenes.[7b] This demonstrated that the six-membered ring of *m*-xylylene retains its aromatic character and its structure is best represented as a triplet biradical as shown in 7.

Photolysis (254 nm) of dibromides (13b–15b) in ethanol at 77 K does not produce the NQM biradicals. We speculate that photolysis of a dibromide leads to cleavage of a carbon–bromine bond to form a radical–atom pair
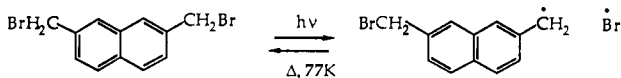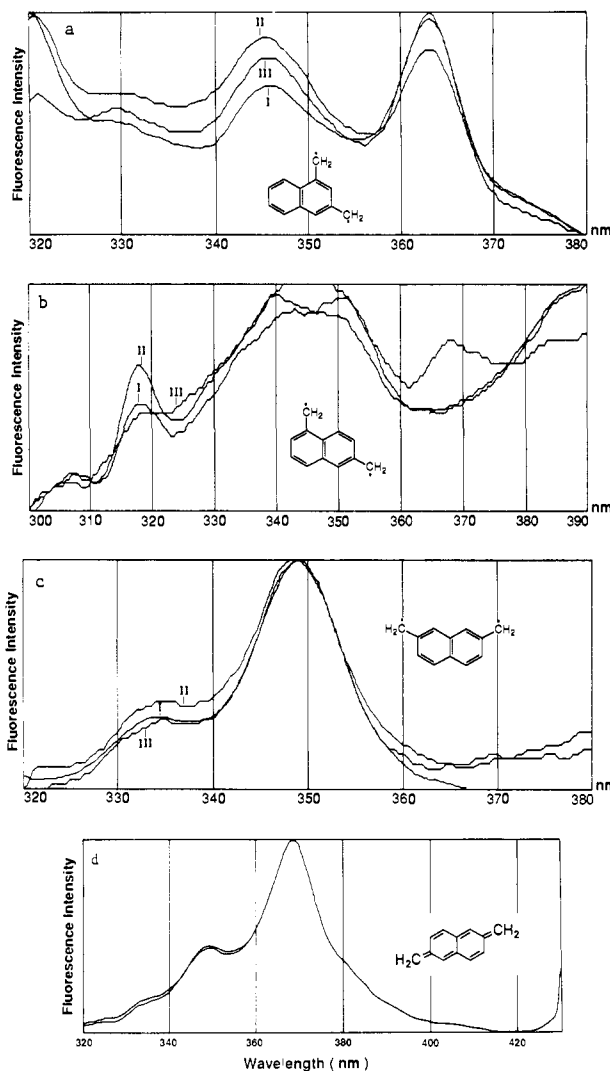
that can rapidly recombine to regenerate the starting material.

Photolysis of a dichloride at 77 K again produces a radical–atom pair, but the chlorine atom of this pair can be scavenged by the matrix (MH).
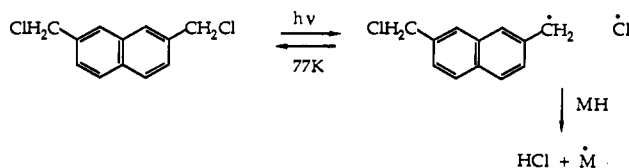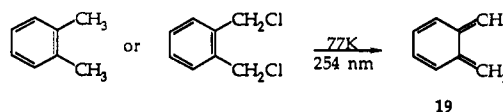
The nascent chlorine atom will abstract a hydrogen atom from the matrix much more rapidly than bromine atoms.[14] Thus,

Figure 2. Fluorescence excitation spectra of (a) **8**, (b) **9**, (c) **10**, and (d) **11**, produced by photolysis (254 nm) of the dichloride precursors (**13a–15a** and **20a**) at 77 K. Monitoring of the fluorescence origin (curve 1) and of the two vibrational bands (curves 11 and 111) is shown.

recombination of the primary radical–atom pair is suppressed with the dichloride precursors. Consistent with this interpretation is the fact that biradical fluorescence spectra were produced from dichlorides 13a–15a only in good hydrogen atom donating matrices (ethanol, 2-MTHF) and could not be obtained when hydrocarbon glasses were employed.

Singlet Biradicaloid 11. *o*-Xylylene (19) has a fluorescence spectrum shifted far to the blue of that of the meta isomer.[7a,b] This emission has a vibrational structure which is very different from that of *m*-xylylene and is most consistent with the singlet ground state, biradicaloid, polyene structure 19.[9] In fact, the emission and excitation spectra of 19 are rather broad and very different in appearance from the relatively well resolved fluorescence spectrum of the *m*-xylylene biradical. The excitation spectrum of 19 is centered between 360 and 400 nm and has a mirror image symmetry relationship with the emission spectrum which is maximized between 440 and 480 nm. The zero–zero transition is at 414 nm. Biradicaloid 19 was first prepared by Migirdicyan by photolysis of *o*-xylene.[7a,b] Haider et al. have shown that photolysis of α,α'-dichloro-*o*-xylene also forms *o*-xylylene.[1,7]

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(12) Gisin, M.; Wirz, J. *Helv. Chim. Acta* **1983**, *66*, 1556.
(13) McClure, D. S. *J. Chem. Phys.* **1956**, *24*, 1.

(14) Bunce, N. J.; Ingold, K. U.; Landers, J. P.; Lusztyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5464.
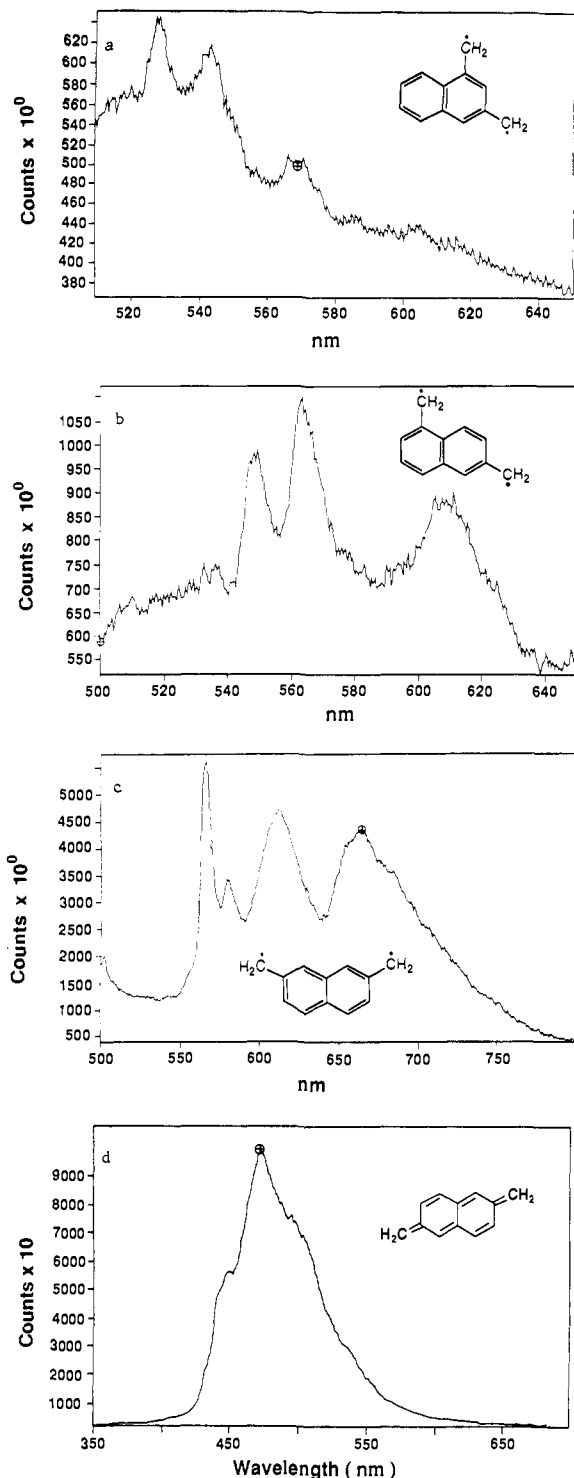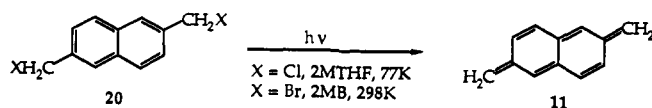
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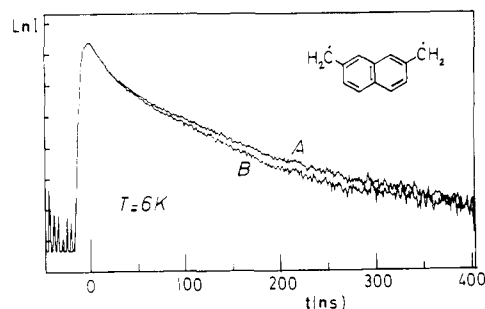
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Figure 4. Fluorescence decays of 2,7-NQM in perdeuterated ethanol at 6 K in the absence (A) and in the presence (B) of a 220-G magnetic field.

the fluorescence spectrum is not observed prior to 254-nm photolysis of dichloride 20a and disappears when the sample is thawed and recooled. The excitation spectrum of the matrix-isolated species is depicted in Figure 2d. The three emission bands produced by low-temperature photolysis of 20 have identical excitation spectra, which is consistent with a single carrier of the fluorescence. The fluorescence spectrum of Figure 1e is at much shorter wavelength than that of the isomeric triplet biradicals 8–10 and is attributed to the singlet 2,6-naphthoquinodimethane biradicaloid 11. The fluorescence spectrum of 11 is much broader than the spectra of triplet biradicals 8–10. The zero–zero band is at approximately 420 nm. The vibrational progression observed in 2,6-NQM is very different from that of triplet biradicals 8–10 (Table I) and is most consistent with the polyene structure depicted in 11. Thus, the fluorescence spectra of 1,3-, 1,6-, 2,7-, and ethano-bridged 1,8-NQM indicate that they are triplet biradicals, whereas the evidence for 2,6-NQM indicates that it is a singlet polyene.

Ambient Temperature Laser-Induced Fluoresence. Exposure of 1,3-, 1,6-, 2,6-, and 2,7-bis(bromomethyl)naphthalenes 13b–15b in 2-methylbutane (2-MB) solution at ambient temperature to KrF excimer laser radiation (249 nm, 100 mJ, 8 ns) produces the laser-induced fluorescence spectra of Figure 3a–d. The spectra produced from the dibromides at ambient temperature contain the spectra generated from the dichlorides at 77 K but are more poorly resolved. They are again attributed to 1,3-, 1,6-, 2,6-, and 2,7-NQM. Apparently the photon flux in a single laser pulse is sufficient to decompose the dibromide precursors and to promote the nascent biradicals and biradicaloid to a fluorescent excited state. It was possible to obtain LIF spectra of 8–10 and 11 at ambient temperature by using the appropriate dichloride precursors, but they were much less intense than the emission obtained with the corresponding dibromides. The LIF spectra of 1,6- and 2,7-NQM are contaminated with the fluorescence of monoradicals between 600 and 700 nm.

Fluorescence Decays. The emission of 2,7-NQM is particularly intense, which prompted us to measure the associated lifetime(s). The emission decay of 2,7-NQM in perdeuterated ethanol at 6 K, excited at 337.1 nm with a nitrogen laser, is nonexponential, as shown in Figure 4. Most of the decay curve is approximated by the sum of two exponentials with component lifetimes of 50 and 150 ns. The third component lifetime of about 10 ns is too close to the laser pulse duration of 6 ns to be unequivocally attributed to the fluorescence of the biradical. The component lifetimes of 50–150 ns are characteristic of spin-allowed transitions, which demonstrates that the emission of 2,7-NQM is indeed a fluorescence. The nonexponential decay observed for 2,7-NQM is attributed to the fluorescence from individual sublevels of its first excited triplet level, as per *m*-xylylene.[16] This interpretation is supported by the significant modification of the decay curve displayed in Figure 4, upon application of a 220-G magnetic field. This magnetic field effect, commonly observed in triplet–triplet

Figure 3. Laser-induced fluorescence spectra (a) 8, (b) 9, (c) 10, and (d) 11 recorded at ambient temperature by flash photolysis (249 nm) of dibromide precursors 13b–15b and 20b in 2-methylbutane.

Photolysis (254 nm) of dichloride 20a in 2-MTHF at 77 K produces a new, strongly emissive species whose fluorescence spectrum is shown in Figure 1e.

X = (a) Cl (b) Br

The spectrum observed is not that of precursor 20 as it is very different from the fluorescence of 2,7-dimethylnaphthalene, which begins at 325 nm and extends only to 400 nm.[15] Furthermore,

(15) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*, 2nd ed.; Academic Press: New York, 1971; p 336.
(16) (a) Lejeune, V.; Despres, A.; Fourmann, B.; Benoist d'Azy, O.; Migirdicyan, E. *J. Phys. Chem.* **1987**, *91*, 6620. (b) Despres, A.; Lejeune, V.; Migirdicyan, E.; Siebrand, W. *J. Phys. Chem.* **1988**, *92*, 6914.

fluorescence, is further evidence that 2,7-NQM is a ground-state triplet biradical.[17]

Conclusions. Very simple levels of theory correctly predict the ground-state multiplicity of *o*-, *m*-, and *p*-xylylene.[4a,6] The work presented herein demonstrates that simple analyses also correctly predict the ground-state multiplicities of the naphthoquinodimethanes. It is even possible to arrive at these conclusions by simply drawing resonance structures. For example, it is possible to draw Kekulé structures for 1,2-, 1,4-, 2,3-, 1,5-, 1,7-, and 2,6-NQM, which are valency-satisfied polyenes. However, it is not possible to draw a resonance structure for 1,3-, 1,6-, 1,8-, or 2,7-NQM, which are not biradical in nature, without recourse to a highly strained tricyclic structure such as **21**. In fact, attempts
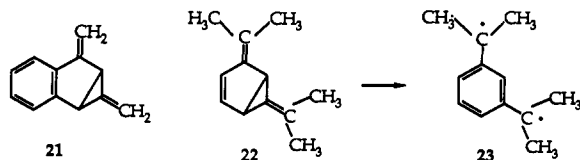
to prepare highly strained bicyclic hydrocarbons of this type (e.g., **22**) have produced *m*-xylylene type biradicals and ultimately dimers derived from it, implying that biradical **23** is more stable than bicyclic triene **22**.[18] Presumably this is also the case as well in the naphthalenic systems.

Experimental Section

Fluorescence measurements performed at 77 K[1] and the laser-induced fluorescence measurements performed at ambient temperature[8] were obtained in the same manner as previously described. Dilute solutions ($\approx 10^{-3}$ M) of a dichloride in 2-MTHF or ethanol are degassed by three freeze-thaw cycles and sealed under vacuum in a quartz tube. The tube was immersed in a dewar containing boiling liquid nitrogen and photolyzed with two Rayonet RPR-2537 lamps for 10–100 s. The dewar was then transferred to a Perkin-Elmer LS-5 spectrofluorometer to obtain emission spectra.

LIF experiments were performed in quartz cuvettes containing samples of dibromides in 2-methylbutane such that their absorbance at 248 nm was approximately 1. The sample was exposed to a single pulse of a Lumonics TE-860-4 laser (KrF, 248 nm). At a 90° angle to excitation the total fluorescence was monitored. The emission was led via a fiber optics cable through a slit (25 μm) onto an Allied analytical systems spectrograph. The dispersed fluorescence was then collected by using a PARC optical multichannel analyzer. The OMA was gated to coincide with the laser pulse. Scattered laser light was removed by the use of a long-pass optical filter.

1,3-, 1,6-, 2,6-, and 2,7-bis(bromomethyl)naphthalene (**13b–15b**) were prepared previously by Reid and Bodem.[19] 2,6-Bis(chloromethyl)-

naphthalene (**20a**) was prepared by the method of Antoun.[20]

1,3-Bis(chloromethyl)naphthalene (13a). 1,3-Bis(bromomethyl)naphthalene (2.34 g, 7.46 mmol) was dissolved in 100 mL of dimethylformamide; 4.06 g (95.8 mmol) of LiCl was added, and the solution was heated with stirring at reflux for 3 h. After the solution cooled, it was poured into 150 mL of water, and then the solution was extracted with hexane (3 × 80 mL). The combined organic layers were dried with anhydrous MgSO₄ and filtered, and then the solvent was removed under reduced pressure to yield a yellow oil which solidified upon standing. The solid was recrystallized in cyclohexane to yield off-white crystals which were purified further by passing through a column (silica gel/cyclohexane) to yield white crystals (0.75 g, 3.33 mmol, 44.7%): mp 61.5–64 °C; H NMR δ 4.75 (2 H, s), 5.05 (2 H, s), 7.52–8.15 (6 H, m); ¹³C NMR δ 44.136, 46.088, 123.605, 126.761, 127.316, 127.876, 128.951, 129.108, 130.813, 133.799, 133.996, 134.273. MS calcd for C₁₂H₁₀Cl₂: 224.0160. Found: 224.0207.

2,7-Bis(chloromethyl)naphthalene (15a). 2,7-Bis(bromomethyl)naphthalene (0.31 g, 0.987 mmol) was dissolved in 50 mL of dioxane. This solution was then added dropwise for 1 h to a stirred solution of 0.35 g of AgNO₃ dissolved in 100 mL of water. The solution was stirred for 2 h, and then the AgBr was filtered. The solution was extracted with ethyl acetate, and the ethyl acetate layers were combined, dried with MgSO₄, and filtered. The solvent was then removed to yield a thick yellow oil which crystallized upon standing to yield crude 2,7-bis(hydroxymethyl)naphthalene which was recrystallized from benzene/methanol to yield white crystals (0.104 g, 0.553 mmol, 56%): mp 113–117 °C; H NMR δ 4.87 (4 H, s), 5.60 (s), 7.49–7.50 (2 H, d), 7.81–7.87 (4 H, m). 2,7-Bis(hydroxymethyl)naphthalene (0.05 g, 0.266 mmol) was stirred with concentrated HCl for 16 h. The solution was filtered through a sintered glass funnel, and the crystals were dried under reduced pressure. The product was purified by column chromatography (silica gel/cyclohexane) to yield white crystals of **15a** (0.05 g, 0.222 mmol, 83.5%): mp 112–115 °C; ¹H NMR δ 4.75 (4 H, s), 7.50–7.54 (2 H, d of d), 7.82–7.86 (4 H, d of d); ¹³C NMR δ 46.381, 126.891, 127.561, 128.516, 135.523, 132.771, 132.957. MS calcd for C₁₂H₁₀Cl₂: 224.0160. Found: 224.0148.

1,6-Bis(chloromethyl)naphthalene (14a). 1,6-Bis(bromomethyl)naphthalene was converted to 1,6-bis(hydroxymethyl)naphthalene as per the 2,7 isomer: mp 58–60 °C; H NMR δ 4.89 (4 H, s), 5.60 (s, 2 H), 7.49–7.50 (d, 1 H), 7.81–7.87 (m, 4 H). The diol was converted to the dichloride as per the 2,7 isomer: mp 77–81 °C; ¹H NMR δ 4.77 (s, 2 H), 5.05 (s, 2 H), 7.42–8.18 (m, 6 H); ¹³C NMR δ 44.325, 46.193, 124.518, 125.955, 127.066, 128.201, 128.358, 129.779, 130.8555, 133.098, 133.800, 135.184. MS calcd for C₁₂H₁₀Cl₂: 224.0160. Found: 224.0153.

(17) The fluorescence decay of 2,6-NQM in perdeuterated ethanol at 8 K is not altered by an external magnetic field, as expected for a ground-state singlet biradicaloid. However, the decay is nonexponential, which is difficult to interpret without additional studies.

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