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Photochemical Generation of 2,3-Naphthoquinodimethane Derivatives. An Extremely Facile "Forbidden" Thermal Reaction and Evidence for a Low-Energy Doubly Excited State

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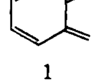
Abstract: The 2,3-naphthoquinodimethanes **5** and **6** are generated by irradiation of the condensed cyclobutenes **7** and **8** in rigid organic glasses at 77 K. Upon warming to about 120 K, **6** rapidly undergoes a "forbidden" electrocyclic ring closure to **8**. If viscosity is low, bimolecular processes contribute to the destruction of **6**. In contrast, **5** is stable in fluid solution up to about 200 K and in a plastic briefly up to room temperature, and its destruction is purely intermolecular, with no detectable return to **7**. UV and PES measurements on **7** and **8** reveal the presence of substantial interactions between the n_+ lone-pair orbital and the σ orbital of the cyclobutene bond formed in the reaction **6** → **8**, and indicate that the striking ease of the "forbidden" ring closure in **6** compared with **5** may be due to similar σ hyperconjugation in the transition state (n_-–σ^* interaction). Another possible contribution is due to the inductive effect of the nitrogens, which makes the "antiaromatic" transition state of the forbidden process look somewhat like a cyclobutadiene dication rather than like unperturbed cyclobutadiene. The UV-visible absorption, linear dichroic, and polarized fluorescence and excitation spectra of **5** and **6** are in excellent agreement with π-electron calculations using singly and doubly excited configurations. Comparison of spectral shapes of the visible bands of **5** and **6** and of their measured radiative lifetimes suggests that an additional very weak low-energy transition is present in **5**. The calculations strongly suggest that this transition largely involves a HOMO,HOMO → LUMO,LUMO double excitation.

Introduction

Highly reactive simple *o*-quinoid hydrocarbons attract considerable current interest. Much of it centers on *o*-quinodimethane (**1**) and related species,[2-9] but 2,3-naphthoquinodimethanes have also been produced as intermediates[10] and isolated in an organic glass at low temperatures.[5,11] Recently, remarkably stable simple derivatives of **1** have been prepared and spectrally characterized (**2**,[5] **3**[6,9b]). In these, the exocyclic carbon atoms of **1** are incorporated in a bulky saturated ring which prevents the orbital symmetry favored conrotatory closure and sterically hinders dimerization and polymerization processes, while exerting a minimum of interference in the electronic structure of the conjugated system. At the same time, the photochemical electrocyclic ring opening in their strained benzocyclobutene precursors is facile, while in benzocyclobutene itself it proceeds only with great difficulty.[2] An extension of the preparative approach which yielded **2** to the *o*-naphthoquinodimethane (**4**) chromophore has already been reported,[5] and a general similarity of band shapes as well as a remarkably large red shift of the first absorption band of the chromophore **4** compared with **1** was noted. In the present paper, we describe in detail our results for two 2,3-naphthoquinodimethane derivatives, **5** and **6**, and compare their spectra and reactivity with those of **2**, and also with the recently published[11] visible spectrum of the parent **4**.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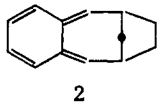
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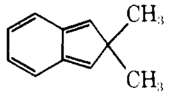

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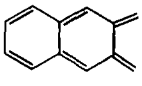
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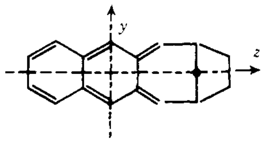

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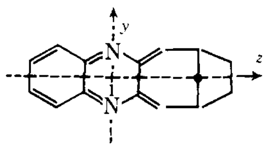

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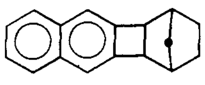
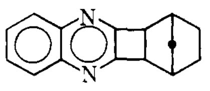
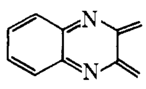

7, exo



8a, endo
b, exo



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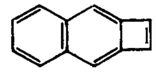
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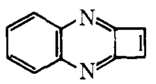

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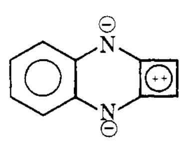

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The naphthoquinodimethanes **5** and **6** were prepared by low-temperature irradiation of the corresponding cyclobutene precursors **7** and **8**, respectively. Similarly as in the case of **2**, the photochemical conversion was only successful when performed in a rigid rather than a fluid solution and is suspected to proceed by subsequent absorption of two photons ($S_0 \rightarrow S_1 \rightarrow T_1 \rightarrow T_x \rightarrow$ product) similarly as proposed for **2** and as proven for the ring opening of some other condensed cyclobutenes.[12,13] Despite the spectral similarities of **2**, **5**, and **6**, several interesting differences between these compounds came to light: (1) **2** is stabilized enormously with respect to **1**, whereas the naphthoquinodimethane **5** is stabilized much less, and the heterocyclic analogue **6** hardly at all; (2) neither **2** nor **5** shows any sign of "Woodward-Hoffmann forbidden" thermal disrotatory electrocyclic reactivity leading to the initial cyclobutene precursor, while in **6** this "forbidden" process is very fast even at −150 °C; (3) the first absorption bands of **5** and **6** are very strongly red-shifted (~200 nm) with respect to that of **2**; and (4) there is reasonable evidence that in **5**, but not **2** or **6**, the doubly excited electronic state, expected to be of low energy in a biradicaloid species,[2,14,15] actually is the lowest excited singlet state of the molecule, as tentatively proposed[11] for **4**.

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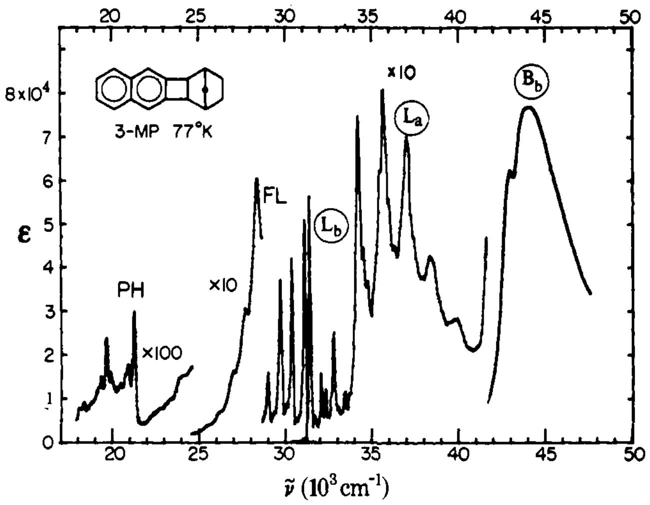

Figure 1. Absorption and uncorrected fluorescence (FL) and phosphorescence (PH) spectra of 7.

Results

The hydrocarbon **7** was prepared by the cycloaddition of 2,3-dehydronaphthalene generated in situ[16] from 2-aminonaphthalene-3-carboxylic acid to norbornene. The assignment of the exo configuration was made by analogy to the reaction of benzyne with norbornene[17] and by examination of the NMR spectrum of **7**. The cyclobutyl methine protons in **7** appeared as a sharp singlet at τ 6.75. The lack of coupling with the bridgehead methine protons is expected only for the exo configuration, where the dihedral angle between the vicinal protons is about 90°. Also, the high observed degree of alignment in stretched polyethylene agrees with the exo assignment (see below).

The preparation of the endo quinoxaline derivative **8a** has been described previously.[5] The thermodynamically more stable exo derivative **8b** could be prepared by distilling **8a** through an unpacked quartz pyrolysis tube maintained at 400 °C (0.05 Torr). Under these conditions, the isomerization was clean and 97% complete. The exo configuration of **8b** was again assigned by examination of its NMR spectrum, which showed the cyclobutyl methine protons as a sharp singlet at τ 6.4, and is also in agreement with the observed degrees of alignment in stretched polyethylene (high for **7** and **8b**, lower for **8a**; cf. Experimental Section). The other spectral data of **8b** were consistently similar to those of **8a**. It seems likely that the isomerization of **8a** to **8b** proceeds via the electrocyclic ring opening of the cyclobutene ring to produce **6**, which then undergoes a ring closure.

The absorption, fluorescence, and phosphorescence spectra of **7** are shown in Figure 1; those of **8a** are shown in Figure 2. Irradiation of vacuum-line degassed fluid solutions of **8a**, **8b**, or **7** in 3-methylpentane (3-MP) at room temperature for up to several hours with a 1-kW Xe lamp and a filter transmitting between 250 and 460 nm yielded no low-molecular weight products, and in particular, no **8a**–**8b** interconversion. In contrast, irradiation of similar but rigid 3-MP solutions of **7**, **8a**, and **8b** at 77 K with the same source or with a 200-W Hg lamp (295-nm cutoff filter) caused rapid disappearance of the absorption and emission spectra of the starting material and their replacement by those of red products, which are stable to further irradiation. From the spectral changes, the degree of conversion in each case can be estimated as at least 90%. The same product is obtained from **8a** or **8b**.

The ordinary and polarized UV-visible absorption, emission, and excitation spectra of the product obtained from **7** are shown in Figure 3; those of the product from **8a** and **8b** are shown in Figure 4. Absolute polarizations were obtained by the stretched sheet method[18] by using the well-known long-axis polarization directions of the L_b transitions in the naphthalene and quinoxaline chromophores to establish the nature of the orientation distribution of the photochemical precursor in stretched polyethylene, then performing the photochemical conversion at 77 K and measuring the resulting dichroic absorptions of the resulting highly aligned rigid solutions of **5** and **6**. In Table I, fluorescence lifetimes and quantum yields, as well as the resulting radiative lifetimes, are compared with the radiative lifetimes calculated from integrated absorption intensities. In each case, we only found evidence for the formation of a single photoproduct (note that excitation spectra duplicate all of the features of the absorption spectra). The extinction coefficients shown were calculated from two independent measurements assuming 100% conversion to a single product. The experimental transition energies, intensities, and polarizations are compared with those calculated by the π-electron PPP method in the figures and in Table II. In the calculations, the electronic effects of the saturated bicyclic moiety, which according to molecular models assures that the π system is planar, were disregarded. Configuration interactions (CI) included doubly excited configurations selected automatically by the systematic SECI-1 procedure of ref 19; parameter values were those appropriate[20] for extensive CI. In Figure 5, absorption, and in Figure 6, photoelectron spectra of **8a** are compared with those of 2,3-dimethylquinoxaline (the spectra of **8a** and **8b** are very similar). The photoelectron spectrum of **7** was essentially identical with that of 2,3-dimethylnaphthalene in the low-energy region except for a ca. 0.1-eV shift to lower binding energies. The two spectra are significantly different in the σ ionization region.

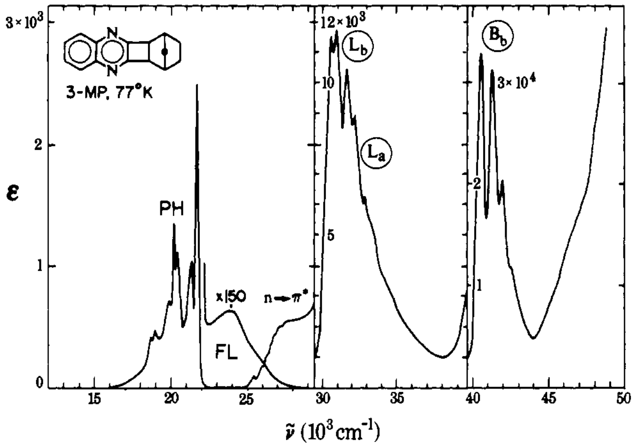

Figure 2. Absorption and uncorrected fluorescence (FL) and phosphorescence (PH) spectra of **8a**. The spectra of **8b** are very similar.

By analogy to the low-temperature photochemical behavior of a variety of polycyclic cyclobutenes which open to the corresponding butadienes,[5,12] the photoproduct from **7** is expected to be **5**; that from both **8a** and **8b** is expected to be **6**. This assignment is supported by the formation of the same product from either **8a** or **8b**, by the striking similarity of the fine structure of the first intense band in the absorption spectra of the products **5** and **6** with that of **2**,[5] and finally by the near superimposability of the visible absorption curve of the product from **7** with that of **4** prepared in a quite different way.[11]

In undegassed samples, warming and melting the matrix cause rapid loss of the new spectra and deposit an apparently polymeric colorless solid, similarly as previously noted[5] for **2**. In carefully degassed solutions, **2** was reported as stable at room temperature.[5] We have now investigated its striking thermal stability further and find that it suffers a loss of less than 10% after 5 h at 80 °C. In remarkable contrast, even in very carefully degassed fluid solutions, the red color of **5** fades

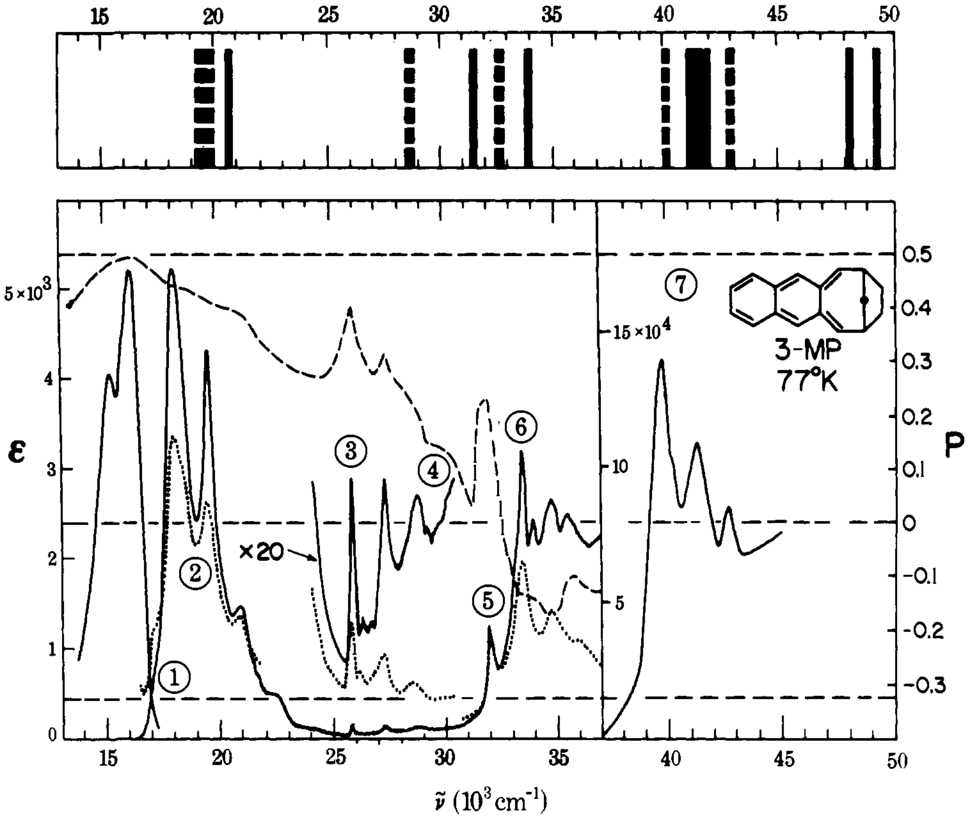

Figure 3. Spectra of **5**: absorption and uncorrected fluorescence (solid), corrected excitation (dotted), and degree of polarization P (dashed). Results of a π-electron calculation are shown on top (broken lines, short-axis polarized; solid lines, long-axis polarized; thickness indicates intensity).

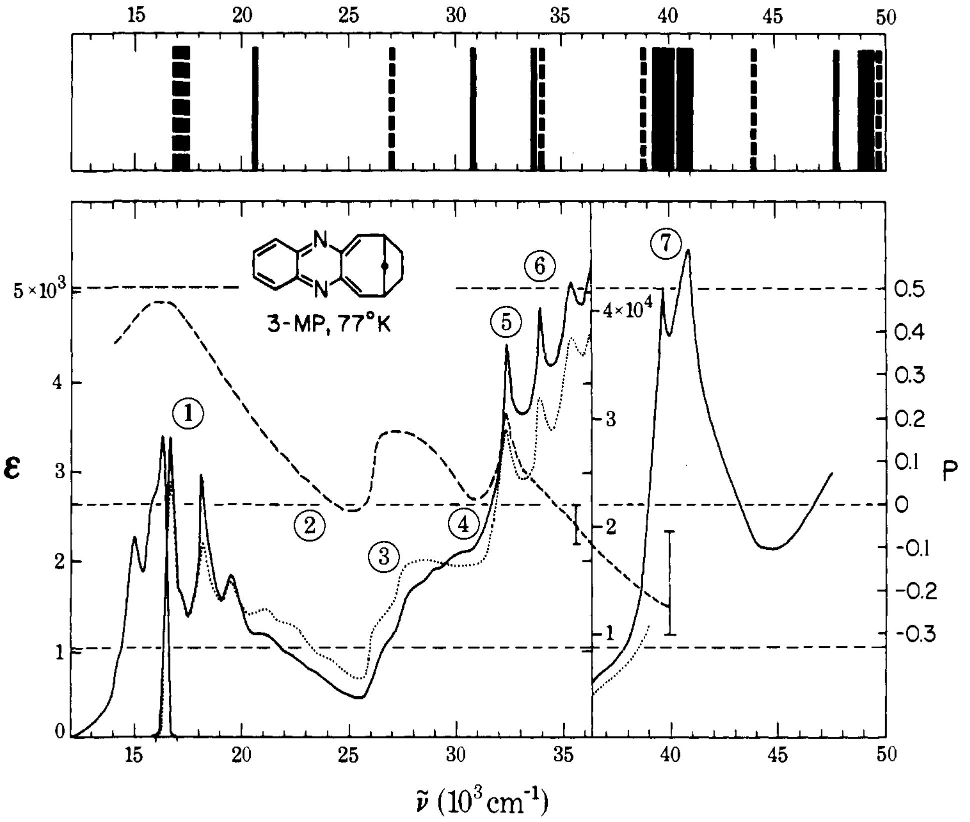

Figure 4. Spectra of **6**. See caption to Figure 3.

at about −75 °C. In degassed poly(vinyl acetate) matrix, it survives briefly at room temperature, while the color of **6** fades at about −150 °C during the warm-up. Both yield an insoluble material reminiscent of the "intractable mixture" reported[11] to result upon the thermal decomposition of an azo precursor of **4** at −40 °C. To our surprise, the warm-up of the solutions of **6** also causes the reappearance of the absorption spectrum of its cyclobutene isomers with 30–40% of the original intensity (the spectra of **8a** and **8b** are virtually indistinguishable). This is true even if the initial photoconversion **8** → **6** is so complete throughout the body of the rigid solution that no detectable **8** remains (irradiation is continued long after the disappearance of the peaks of **8** in absorption, and of its characteristic blue emission, and the sample cell is realigned repeatedly in the Dewar vessel to ensure complete conversion in all corners). The reappearance of **8** is unmistakable in the absorption as well as emission spectra. When such a solution is refrozen and irradiated, the absorption and emission spectra of **6** reappear more weakly, and after several such cycles no **6** or **8** is detectable. In the case of **5**, no analogous thermal conversion to **7** is observed, although the sharp absorption bands of **7** would make it easier to detect. Since the same experimental techniques were used for **5** and **6**, this result also makes it clear that the observed reappearance of **8** is not due to traces of unconverted starting material in the corners of the sample cell surviving the initial conversion **8** → **6**. Partial return of **6** to **8** occurs also in a carefully degassed poly(vinyl acetate) matrix, which is very highly rigid at the low temperatures required, leaving no doubt that the process is unimolecular.

Discussion

Spectroscopy of the Naphthoquinodimethanes 5 and 6. The absorption spectra of **5** and **6** are quite similar. Both are characterized by a visible band of medium intensity and pronounced vibrational structure similar to that of **2**, followed by a series of less distinct bands in the region 25 000-35 000 cm^{-1} and by a very strong band near 40 000 cm^{-1}. Inspection of the absorption and polarized emission curves permits an assignment of individual electronic transitions as shown in Figures 3 and 4 and summarized in Table II, along with the absolute polarization directions obtained from stretched sheet measurements. All three groups of absorption bands are correctly predicted by the π-electron calculations, which also account very well for the absolute transition polarizations, for the enormous red shift of the first bands in **5** and **6** as compared with **2**, as well as for the small but distinct red shift of the first strong absorption peak in **6** compared to **5**.

The near superimposability of the structured visible absorption band of **5** with that of **4**[11] is striking; the ~400-cm^{-1} red shift in **5** can be attributed to the alkyl substituents. It is interesting to note that a similar agreement of excitation energies is found in the pair **1** and **2**, but that their band shapes are quite different: that of **1** is Franck-Condon forbidden[2] and the 0-0 peak is very weak both in absorption and in emission,[8] whereas that of **2** is Franck-Condon allowed, with both 0-0 peaks quite strong.[5] This difference has been tentatively attributed[5] to imperfect planarity of **1** in its ground-state S_0 due to steric interference of the inside hydrogens of the exocyclic methylene groups, and much increased or perhaps perfect planarity in the first excited singlet state S_1. In **2**, as well as **5** and **6**, planarity in both states is assured by the rigid polycyclic structure and leads to a Franck-Condon allowed shape for the first intense transition. The close similarity in the shapes of the first intense band in **4** and in the rigid derivative **5** makes it likely that **4** also is planar in the ground as well as the excited state. The cause of the difference in the degree of planarity of the S_0 state of **1** (presumably with one methylene above, the other below the ring plane) and the S_0 state of **4** (planar) is likely to be the same as that of the difference between the S_0 state of **1** and its planar S_1 state: increased conjugation in the latter, reflected in a higher bond order of the formally single ring bond between the two vinylidene groups, making twisting around it harder, and in a lower bond order in the exocyclic bonds of the vinylidene groups, making them longer and reducing the steric interactions of the inside hydrogens. The pronounced progression in a ca. 1500-cm^{-1} vibration which is present in all six cases (**1**-**6**) can be reasonably attributed to an in-plane skeletal vibration, associated with the change in equilibrium bond lengths upon $S_0 \rightarrow S_1$ excitation, compatible with calculated changes in bond orders (cf. ref 2). The shoulder seen on the long-wavelength side of the first absorption band of the parent **4** also appears in our spectrum of **5**. In **6**, this weak shoulder is absent and the Franck-Condon allowed structure of the first band is quite clear.

Table I. Fluorescence Characteristics of **5** and **6**[a]

	Φ_{fl}	τ_{fl}, ns	$\tau_{\mathrm{rad.}}$, ns	$\tau_{\mathrm{rad.}}^{\mathrm{calcd}}$, ns
5	0.018	4.5	250	67
6	0.018	3	170	85

[a] Errors are estimated. The experimental uncertainty in the relative values of Φ_{fl} is ~±5%, but the absolute magnitudes are subject to an unknown uncertainty in the value published for the standard. The experimental uncertainty in the relative values of τ_{fl} is estimated at ~±20%; the absolute error is ~±1 ns.

In view of the excellent general agreement among calculations and experimental energies, absolute polarizations and relative intensities, the calculated near degeneracy of the first excited singlet state probably corresponds to reality. The calculated short-axis polarized relatively intense transition should correspond to HOMO → LUMO excitation and its properties fit well the observations. The other transition should correspond approximately to a double HOMO,HOMO → LUMO,LUMO excitation, which should be extremely weak and long-axis polarized. It has been already suggested that the weak shoulder in **4** is due to the transition into the doubly excited state.[11] In contrast to expectations, our polarization data show that the absorption intensity in the region of the shoulder carries the same polarization as the allowed HOMO → LUMO excitation. If the intrinsic oscillator strength for the doubly excited state is negligible as suggested by the calculations, this does not contradict the proposed assignment: all of the observed intensity is borrowed either by an intramolecular vibronic mechanism or by intermolecular site effects; the latter could account for the fact that no change in the polarization is observed even at the longest wavelengths where the 0-0 band is presumably located. A similar situation has been recently reported for linear polyenes.[21] Additional evidence was sought from a comparison of measured radiative lifetimes with those calculated from absorption spectra. While in **5** the measured lifetime is definitely longer than that expected if all of the first absorption band corresponded to only one transition and in **6** the discrepancy is within a not uncommonly observed factor of two, the difference is too small to be convincing. In the absence of unequivocal support from the polarization and lifetime measurements, the best evidence for the assignment of the weak shoulders in **4** and **5** to the doubly excited state is provided by the comparison of the spectra of **5** and **6**. In **6**, the strong transition is calculated to be red-shifted by about 2000 cm^{-1} compared with **5**, while the weak transition should not be shifted, so that it should then be buried under the strong one. Indeed, the shoulder is missing in the spectrum of **6**. In view of the closely similar geometries of the two compounds, it is difficult to account for this difference in another way.

The doubly excited state is likely to be a carrier of photochemical reactivity such as electrocyclic ring closure and twisting around double bonds, and to produce little if any fluorescence when it is the lowest excited singlet. The reversal in the order of HOMO → LUMO and "$\mathrm{HOMO}^2 \rightarrow \mathrm{LUMO}^2$" states could then account for the striking difference between the strongly fluorescent **1** and nonfluorescent[11] **4**. In **5**, chemical transformations are hindered by the polycyclic ring structure, and fluorescence is restored, although the doubly excited state is lowest. If this reasoning is correct, **9** should be fluorescent, since its state ordering is the same as that in **1**.

Table II. Excited States of **5** and **6**[a]

	exptl			theor			
	E_n	f	pol	E_n	f_r	pol	f_p
5							
1	17.0	0.05	y^b	20.8	0	z	0
2	18.0		y	19.7	0.18	y	0.21
3	25.9	0.002	y	29.0	0	y	0
4	~29.4		z	31.8	0	z	0
5	31.4	0.06	y	33.0	0.0001	y	0.001
6	33.6		z	34.3	0	z	0
				40.1	0	y	0
7	39.6	2	z	41.5	1.6	z	1.5
6							
1	16.5	0.05	y	17.3	0.1	y	0.1
2	~20–25		z	20.6	0.03	z	0.03
3	26.0	0.05	y	27.3	0.04	y	0.02
4	~30		z	31.1	0.02	z	0.03
5	32.4	0.1	y	34.4	0.05	y	0.05
6	~34		z	33.8	0.01	z	0.01
				38.9	0.05	y	0.04
7	39.7	0.9	z	40.1	1.2	z	1.1
				41.1	0.15	z	0.16

[a] Energy (10^3 cm^{-1}), oscillator strength (f), and polarization (pol) in the axis system of formulas **5** and **6** are given. Oscillator strengths were calculated using both the dipole length (f_r) and dipole velocity (f_p) formalisms. [b] Presumably borrowed.

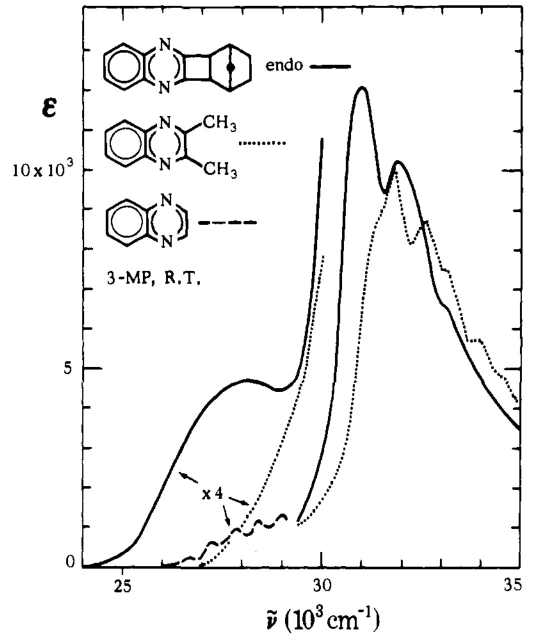

Figure 5. The n-π* absorption region of quinoxaline, 2,3-dimethylquinoxaline, and **8a** (**8b** is very similar to **8a**).

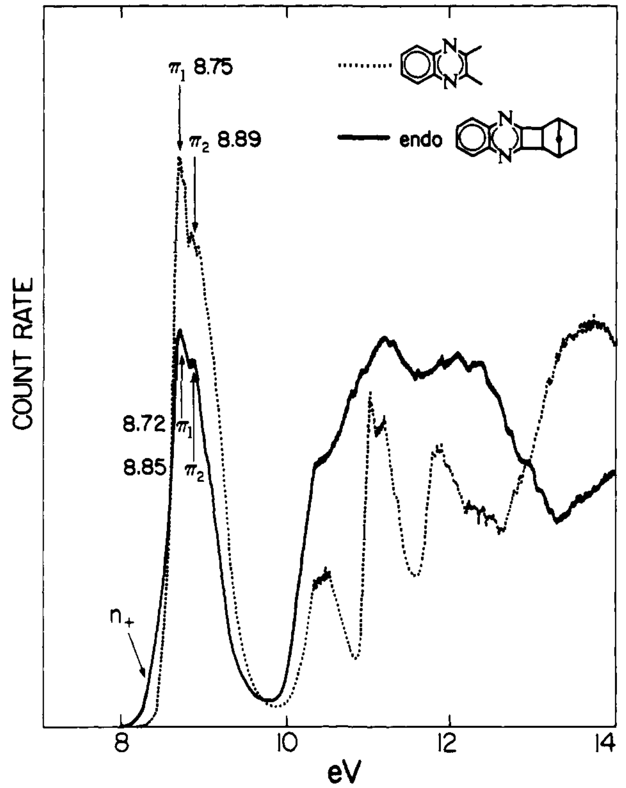

Figure 6. Photoelectron spectra of **8a** and 2,3-dimethylquinoxaline, with assignment of the first two π ionizations and the n₊ ionization in **8a** (in quinoxaline, n₊ is believed to be buried under the π_1 and π_2 ionizations).

Reactivity of the Naphthoquinodimethanes 5 and 6. Both **5** and **6** are very much more reactive than **2** and illustrate the limits of the bimolecular stability conferred on an *o*-quinoid hydrocarbon by the device of attaching a bulky moiety. The increased reactivity is anticipated from the availability of a large choice of dimerization sites, from the less sterically hindered nature of some of them, from the increased exothermicity of those processes which restore the aromatic rings, and from the decreased HOMO-LUMO gap. The last mentioned point is related to the theoretically expected much more biradicaloid nature of the π-system **4** compared with **1**, which is reflected also in the much lower excitation energy of the former (in the Hückel approximation, the HOMO-LUMO separation is 0.59β in **1**, 0.34β in **4**, and 0 in a "perfect" biradical).

The striking difference between the reactivity of **5** and **6**, which has two fewer dimerization positions but dimerizes or oligomerizes at much lower temperatures, is harder to understand. While the PPP calculation predicts an even smaller HOMO-LUMO energy difference in **6** than in **5**, in agreement with the somewhat lower energy for the HOMO → LUMO excitation (first intense transition) in **6**, it could have been hardly expected that this relatively small change would cause the dramatic difference actually observed.

Perhaps the most puzzling observation is the high rate at which **6** unimolecularly rearranges to **8** at −150 °C, given that **5** does not yield **7** even at room temperature, and that **2** does not cyclize at 80 °C. We have not been able to perform a kinetic measurement of the disappearance of **6**, but there is no doubt that the unimolecular rate constant for its ring closure at −150 °C is of the order of 0.01 s^{-1} or higher. For frequency factors log A = 10–16, this corresponds to activation energies of at most about 7–10 kcal/mol. On the other hand, the constant for ring closure of **5** at 25 °C is certainly less than 0.01 s^{-1}, corresponding similarly to activation energies of at least 16–25 kcal/mol. Perusal of molecular models indicates that there is no low-energy reaction path for the **6** → **8** conversion which would avoid a very considerable cyclic overlap of the four orbitals involved in the electrocyclic process, certainly not with small enough strain to permit such a rapid reaction at −150 °C. Thus, the conversion has to be viewed as a pericyclic (concerted) process, even if the path of lowest energy is such that one of the two CH groups rotates a little ahead of the other. We find this extremely facile "symmetry forbidden" reaction **6** → **8** rather unusual, in spite of the following considerations: (1) certain thermal disrotatory electrocyclic cyclobutene ring openings to 1,3-butadienes and butadiene ring closures to cyclobutenes are known to proceed rapidly near room temperature (activation energies in kilocalories/mole): bicyclo[2.1.0]pent-2-ene → 1,3-cyclopentadiene,[22] 26.9; 2-methylbicyclo[2.1.0]pent-2-ene → 2-methyl-1,3-cyclopentadiene,[23] 24.7; 5,5-dimethylbenzobicyclo[2.1.0]pent-2-ene → 2,2-dimethylisoindene,[6] 18.9; 7,12-dimethylpleiadene → 6b,10b-dimethyl-6b,10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene,[24] 21.3); (2) other things being equal, an increase in the biradicaloid nature of the starting material should decrease the difference between its allowed and forbidden reaction rates;[12] (3) a "symmetry-forbidden" reaction can in principle have any activation energy since the theory only states that the "forbidden" process will have a higher activation energy than an otherwise similar "allowed" process.

The most intriguing aspect of the observed reactivities is the huge difference between **5** and **6**, for which we can offer two rationalizations in the hope that one or both are relevant. The first one is based on the presence of nitrogen lone pairs in **6**. σ hyperconjugation has been recognized as a structure-influencing factor in a variety of bonding situations (e.g., the anomeric effect in sugars[25]) and more recently also as a rate-influencing factor (e.g., the differential kinetic acidity of diastereotopic protons α to a sulfonium function[26]), and it could be responsible for the great ease of the process **6** → **8**, if in the transition state the n_- combination of lone pairs is stabilized by interaction with the empty σ^* orbital of the newly forming bond. Experimental evidence for the existence of a similar n–σ interaction in **8** itself is seen in Figure 5: the $n_+ \rightarrow \pi^*$ transition of **8a** is located about 7 kcal below that of 2,3-dimethylquinoxaline, which represents a reasonable interaction-free model (the shift in **8b** is similar). It is quite well established that in azanaphthalenes the relative values of the energy of the n–π^* transition reflect faithfully those of the energy difference between the n and π^* orbitals.[27] In photoelectron spectra (Figure 6), the difference between 2,3-dimethylquinoxaline and **8** is less clear-cut, since in the former, the peak of the n_+ ionization is apparently hidden below the merging bands of the first two π ionizations, so that its exact energy cannot be determined, similarly as in quinoxaline[28] (cf. the virtual superimposability of the low-energy regions in the photoelectron spectra of **7** and 2,3-dimethylnaphthalene). In **8**, the n_+ ionization probably corresponds to the indistinct shoulder on the low-energy side of the first π ionization and thus indeed appears to be shifted to lower energies with respect to 2,3-dimethylquinoxaline as would be expected from the UV results, but the magnitude of the shift is unknown. This shift cannot be attributed to ring strain: fusion of the four-membered ring will decrease the angle C_9–C_1–C_2 and thus provide the n orbitals with increased s character and increased ionization potentials (for a detailed discussion of related systems, see ref 29). In **8**, the interaction of n_- with σ^* would be expected to be much weaker because of their large energy separation. However, in the transition state for the reaction **6** → **8**, the newly developing σ and σ^* orbitals are both nearly nonbonding, and thus more favorably located for stronger interaction with the n_+ and n_- orbitals.

Another rationalization of the huge difference between **5** and **6** is based on the Dewar-Zimmerman theory of pericyclic reactions.[30] If we take 2,3-naphthocyclobutadiene **10** as the model of the transition state for the ring closure in **5** and its diaza derivative **11** as the corresponding model for **6**, some differential stabilization of the transition state corresponding to **6** is expected by relief of antiaromaticity by shifting electron density from the cyclobutadiene ring on the two nitrogens in the sense of the valence bond structure **12**. A simple Hückel calculation along the lines of ref 31 predicts a stabilization by 0.041β, but this appears to be much too little to account by itself for the huge difference between the reactivity of **5** and **6**: we estimate β at roughly 20 kcal/mol from the fact that the activation energy for disrotatory ring opening of bicyclo[2.1.0]pent-2-ene is lowered by 8 kcal/mol upon benzo annelation,[6] and this should correspond to 0.38β. Of course, it is possible that the cyclobutadienes **10** and **11**, in which HOMO and LUMO are not degenerate, are relatively poor models for the transition state which may actually lie closer to the point along the reaction coordinate where LUMO and HOMO cross, i.e., are degenerate.

In summary, the difference between **5** and **6** remains intriguing, and if a similar effect can be found in a smaller model system, it would appear to be worth a more detailed theoretical study.

Experimental Section

***exo*-Naphtho[*b*:3,4]tricyclo[4.2.1.0^{2,5}]nonane (7).** A 500-mL flask was charged with 3.76 g (40 mmol) of norbornene in 80 mL of 1,2-dichloroethane and 1.93 mL of isoamyl nitrite. The solution was heated to reflux and a solution of 935 mg (4 mmol, 80%) of 2-aminonaphthalene-3-carboxylic acid (Aldrich) in 150 mL of 1,2-dichloroethane was added over 5 h. The mixture was heated an additional 3 h and the solvent removed under vacuum. The residue was extracted with hot ether and the ether-soluble portion was chromatographed on 30 g of neutral alumina(IV) using pentane. In this manner, 200 mg of a white crystalline solid was obtained: mp 87–91 °C; ^{1}H NMR (CCl_4) τ 2.4 (m, 2 H), 2.72 (m, 4 H), 6.75 (s, 2 H), 7.7 (m, 2 H), 8.48 (m, 2 H), 8.83 (m, 2 H), and 9.17 (br s, 2 H); IR (CCl_4) 3050, 2950, 2860, 1500, 1430, 1310, 1290, 1190, 1160, 1080, 890, and 860 cm^{-1}; UV (C_6H_{12}) λ_{max} 260 (4793), 268 (7100), 278 (8300), 290 (5900), 308 (1800), 312 (1200), and 320 (2950); mass spectroscopic mol wt 220.124, for $C_{17}H_{16}$ calcd 220.1256.

Preparation of the Endo Quinoxaline Derivatives (8a) of *endo*-Tricyclo[4.2.1.0^{2,5}]nonane-3,4-dione. This material was prepared in 82% yield as previously described:[5] mp 104–106 °C; ^{1}H NMR ($CDCl_3$) τ 2.03 (m, 2 H), 2.39 (m, 2 H), 5.93 (m, 2 H), 7.27 (m, 2 H), 8.16 (m, 2 H), and 8.4–9.2 (m, 4 H). The chemical shifts reported in ref 5 were in error.

Preparation of the Exo Quinoxaline Derivative (8b). The quinoxaline derivative **8a** (100 mg) was distilled (bath 130 °C) through a quartz pyrolysis tube (36 × 3 cm) maintained at 400 °C (0.04 mm). A yellowish brown liquid collected in the trap (−78 °C) which solidified upon standing (95 mg). This material was further purified by TLC (silica gel, 85:15 hexane–ether) to yield a colorless white solid: mp 98–100 °C; ^{1}H NMR ($CDCl_3$) τ 1.97 (m, 2 H), 2.37 (m, 2 H), 6.4 (s, 2 H), 7.27 (br s, 2 H), and 8.03–9.3 (m, 6 H); IR (CCl_4) 3060, 2960, 2870, 1515, 1450, 1350, 1290, 1280, 1180, 1130, 1100, and 1015 cm^{-1}; mass spectroscopic mol wt 222.115, for $C_{15}H_{14}N_2$ calcd 222.1157.

Irradiation of 7 and 8a in Rigid Polymer Matrices. A stock solution was prepared by dissolving 3.0 g of poly(vinyl acetate) in 27 g of distilled THF. This solution was then diluted ½ and used to dissolve the photoactive materials.

8a (2.0 mg) was dissolved in 10 mL of the stock polymer solution, which was then carefully freeze–thaw degassed to <1 μm. The solution was then tipped into a perpendicular side arm to which was attached a 1-cm quartz cuvette. The solvent was pumped off leaving a thin film on the walls of the cuvette. The degassed polymer film was then irradiated with a 200-W Hg-Xe lamp using a Pyrex filter at 77 K for 1 h. After this time ca. 35% of the starting material had been converted and the film had a faint purple cast. When this material was warmed to room temperature and recooled for spectral analysis, it showed 90% of the original optical density of the starting material had been recovered. Increased irradiation times or the use of more concentrated solutions led to the regeneration of less starting material upon warm-up.

7 (2.0 mg) was dissolved in 10 mL of the stock polymer solution and a degassed film prepared as described above. This film was irradiated at 77 K for 1 h. UV monitoring indicated 60% conversion at this point. When the sample was removed and warmed to room temperature, the color slowly faded. Even after 5 min at 25 °C, the film was still faintly colored. After 15 min at room temperature, the film was recooled to 77 K and the spectrum recorded. Under these conditions, no re-formation of starting material could be detected.

Measurements. UV-Visible, Absorption and Emission Spectra, Linear Dichroism. Low-temperature photochemical transformations were performed and absorption spectra were taken as described in ref 12. Low-temperature stretched sheet measurements were performed as in ref 32. The L_b transitions of the exo isomers **7** and **8b** showed strong positive dichroism. The alignments of the long axis, expressed as the average of the square of the direction cosine, $\langle \cos^2 \beta \rangle$, were 0.57 and 0.53, respectively (0.33 corresponds to a random distribution). The endo isomer **8a** showed a much weaker positive dichroism for the long-axis polarized L_b transition, $\langle \cos^2 \beta \rangle = 0.39$, and thus was less suitable for absolute polarization studies. These numbers are in good agreement with expectations based on molecular shapes.[18] After partial conversion to the photoproducts, negative dichroism was observed for the visible transitions of both **5** and **6**. Starting with the exo isomers, the alignment of this transition moment was very pronounced, and $\langle \cos^2 \beta' \rangle$ was 0.16 for **5** and 0.19 for **6**. Starting with the endo isomer **8a**, the alignment for **6** was much less pronounced but still clearly away from the stretching direction (0.28). These results leave no doubt that the visible transition in **5** and **6** is short-axis polarized. At the same time, strongly positive dichroism of the intense UV transition near 40 000 cm^{-1} in both **5** and **6** prepared from the exo cyclobutenes **7** and **8b** showed that this transition is long-axis polarized. Polarizations of all other transitions were established relative to those absolute results by use of polarized fluorescence emission and excitation spectra. The polarized excitation spectrum of **5** in the region of very weak absorption around 16 500 cm^{-1} was determined using a Chromatix CMX-4 flash lamp pumped dye laser as the excitation source. The light from the laser was depolarized using a polarization scrambler, and then the degree of emission polarization was determined using the usual polarizer assembly. There was no evidence for any change of the polarization in the very weak absorption toward longer wavelengths relative to the more intense absorption around 18 000 cm^{-1}. Emission spectra were measured using equipment and procedures described in ref 33. Fluorescence quantum yields of **5** and **6**, Φ_{fl}, were estimated by comparison of the integrated emission intensities with that of a room temperature solution of oxazine 170 in ethanol. The fluorescence quantum yield of oxazine was taken to be 0.5.[34] Emission intensities were measured at an angle of 14.5° from the excitation direction. No corrections were made for directional emission anisotropy. Also, no corrections were made for the variations in instrumental response over the fluorescence energy range, since the energy range over which the oxazine emits is similar to that over which compounds **5** and **6** emit.

The fluorescence lifetimes of **5** and **6** were measured by exciting the samples with a Molectron UV-1000 pulsed nitrogen laser pumped dye laser at 560 nm (Coumarin 540A) and measuring the fluorescence decay. The fluorescence was detected through a ¾ m Spex 1702 monochromator with a 1P28 photomultiplier and displayed on a Tektronix 7844 oscilloscope. The dye laser pulse was observed to have a width of 6 ns fwhm and the lifetimes of fluorescence emissions were determined by deconvolution. Theoretical radiative lifetimes, $\tau_{rad.}{}^{calcd}$, were calculated from integrated absorption using the relation:[35]

$$\tau_{rad.}{}^{calcd} = \left[2.88 \times 10^{-9} n^2 \int \frac{(2\bar{\nu}_0 - \bar{\nu})^3}{\bar{\nu}} \epsilon(\bar{\nu})\, d\bar{\nu}\right]^{-1}$$

where ν_0 is the wavenumber of mirror symmetry between emission and absorption. The refractive index of the solvent, n, was taken to be 1.5.

Photoelectron spectra were measured on a Perkin-Elmer PS16 spectrometer.

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