

## 85. Conjugated Biradical Intermediates: Spectroscopic, Kinetic, and Trapping Studies of 2,2-Dimethyl-1,3-perinaphthadiyl

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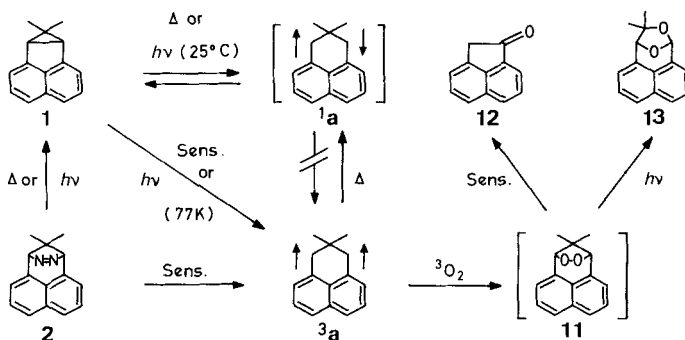
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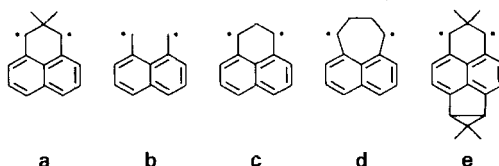
The biradical 2,2-dimethyl-1,3-perinaphthadiyl (**a**) was generated from two different precursors, the naphthocyclopropane **1** and the azo compound **2**, and from each by three different pathways (pyrolysis, direct photolysis, and triplet sensitization, *Scheme 1*). The combined evidence from flash photolysis, low-temperature spectroscopy, and product analyses provides a detailed mechanistic picture of the formation and decay of this reactive intermediate which is persistent at 77 K in the triplet ground state ( $^3\mathbf{a}$ ) and rather long-lived (400  $\mu\text{s}$ ) at room temperature. When formed in its lowest singlet state ( $^1\mathbf{a}$ ), the biradical is too short-lived to undergo intersystem crossing to  $^3\mathbf{a}$  or bimolecular reactions. Thus,  $^3\mathbf{a}$  is formed exclusively from the excited triplet state of the precursor compounds,  $^3\mathbf{1}^*$  or  $^3\mathbf{2}^*$ . The monomolecular decay of  $^3\mathbf{a}$  is retarded by the spin barrier;  $^3\mathbf{a}$  initiates the polymerization of acrylonitrile and is trapped by  $^3\text{O}_2$ .

**Introduction.** – Biradicals may be qualified as the most commonly invoked and least understood reactive intermediates in organic (photo-) chemistry. Their potential as bifunctional reactants has hardly been exploited for designed syntheses [1], and direct evidence concerning their physical properties and chemical reactivity remains scarce [2]. Their lowest electronic state may be either of singlet or triplet multiplicity and, depending on the spin state, the chemical behaviour may be expected to be widely different. The predictability of biradical behaviour then hinges on a knowledge of the multiplicity of the reactive species formed and the rates of intersystem crossing (ISC) connecting its thermally accessible states [3] [4].

The present work provides such detailed information for a selected model system, 2,2-dimethyl-1,3-perinaphthadiyl (*2,3-dihydro-1H-1,3-phenalenediyl*; **a**), which was formed by various pathways from two different precursor compounds, **1** and **2** (*Scheme 1*). Several related 1,8-naphthoquinodimethane biradicals (**b** to **e**) have been studied

Scheme 1. Formation and Trapping of the Biradical **a**

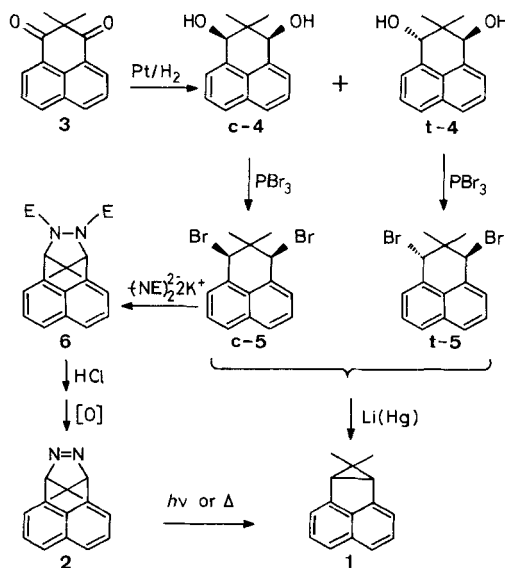




during the last decade [5–16]. The triplet ground state of these metastable intermediates has been characterized by various spectroscopic methods, but little is known about the mechanism of formation and decay of these species and the role of their counterparts of singlet multiplicity. Thanks to the strong and characteristic absorption bands of naphthoquinodimethanes, these systems are ideal for time-resolved studies by flash photolysis.

**Results and Discussion.** – *Synthesis of the Precursor Compounds 7,7-Dimethyl-6b,7a-dihydro-7H-cycloprop[a]-acenaphthylene (1) and 1,4-Dihydro-1,4-isopropylidenenaphtho[1,8-de][1,2]diazepine (2).* The synthesis of the azo precursor **2** by conventional methods, which had failed to provide an azo precursor to **c**, was possible due to the dimethyl blocking group. The preparative work is summarized in *Scheme 2*, details are given in the *Exper. Part*. Two different syntheses have been reported for 2,2-dimethyl-2,3-dihydrophenalene-1,3-dione (**3**). Having used both, we find the three-step procedure [17] starting from 1,8-naphthalic anhydride more convenient, since it avoids the cumbersome separation of isomers formed by the direct *Friedel-Crafts* synthesis [18].

Scheme 2. Synthesis of the Precursors **1** and **2**

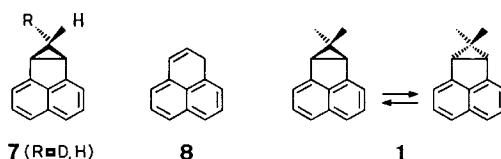


*Isodynamical Ring Inversion of t-4 and t-5.* The *trans*-isomers of the diol **4** and of the dibromide **5** both exhibited broad  $^1\text{H-NMR}$  spectra at room temperature due to the inversion of the fused cyclohexene ring. Coalescence of the  $\text{CH}_3$  signals occurred at  $T_c \cong 270\text{ K}$  ( $\Delta\delta = 0.84\text{ ppm}$ ) and  $T_c \cong 295\text{ K}$  ( $\Delta\delta = 0.57\text{ ppm}$ ), respectively, on a 90 MHz spectrometer ( $\Delta\nu = 90 \cdot \Delta\delta\text{ s}^{-1}$ ). Using the simple relationships for the rate constant

$$k(T_c) = \Delta\nu \cdot \pi / \sqrt{2} = (k_B T_c / h) \exp(-\Delta G^\ddagger / RT_c),$$

the barriers to ring inversion may be estimated as  $\Delta G^\ddagger(t-4) \cong 54\text{ kJ/mol}$  and  $\Delta G^\ddagger(t-5) \cong 60\text{ kJ/mol}$ .

*Photolysis and Pyrolysis of 1 and 2.* The hydrocarbon **1** proved to be relatively stable to irradiation both in degassed and aerated solution at room temperature; slight changes in the absorption spectrum of **1** became apparent only after the absorption of more than 100 photons (313 nm) per molecule. This was of great advantage for the photophysical and mechanistic studies described below. The much more rapid photoconversion of the non-methylated naphthocyclopropane **7** (R=H) to phenalene (**8**), which in turn gave rise to complex reactions, had hampered both trapping [14] and flash spectroscopic [19] studies of the biradical c.



Roth and Enderer [5] have determined the activation parameters  $E_a = 146 \pm 2$  kJ/mol and  $\log(A/s^{-1}) = 14.9$  for the epimerization of *exo*-monodeuterated naphthocyclopropane (**7**, R=D), and Pagni *et al.* [14] have established by further labelling studies that this reaction proceeds by cleavage of the fused cyclopropane C–C bond, *i.e.* via c. An attempt to observe the coalescence of the CH<sub>3</sub> signals in the <sup>1</sup>H-NMR spectrum of **1** due to isodynamical ring inversion has failed; rapid decomposition occurred above 170 °C in (D<sub>7</sub>)-1-chloronaphthalene and no signal broadening was found up to this temperature on a 90 MHz spectrometer.

The azo compound **2** was cleanly converted to **1** both by pyrolysis and photolysis. The thermal reaction proceeded slowly at room temperature in the dark and an Arrhenius plot of the first-order reaction rates, determined spectrophotometrically with CH<sub>2</sub>Cl<sub>2</sub> solutions in the temperature range of 25 to 38 °C (Table), gave the following activation parameters:  $E_a = 105 \pm 1$  kJ/mol,  $\log(A/s^{-1}) = 14.1 \pm 0.2$ . A photochemical quantum yield  $\phi(\mathbf{2} \rightarrow \mathbf{1}) = 1.2 \pm 0.1$  was determined for 365 nm irradiation with an Aberchrome 540 actinometer [20].

Table. Collection of Temperature-Dependent Data

| $T/K$ | $k_{-N_2} \cdot 10^4/s^{-1a)}$ | $T/K$ | $A_0(^3a)^c)$ | $T/K$ | $\tau(^3a)/ms^d)$ |
|-------|--------------------------------|-------|---------------|-------|-------------------|
| 298.2 | 0.447                          | 246.1 | 0.063         | 240.3 | 7.86              |
| 302.8 | 0.873                          | 249.3 | 0.061         | 243.1 | 6.56              |
| 306.8 | 1.514                          | 252.0 | 0.055         | 246.1 | 5.45              |
| 311.4 | 2.743                          | 254.7 | 0.052         | 249.3 | 4.40              |
|       |                                | 258.3 | 0.047         | 252.0 | 3.87              |
|       |                                | 261.5 | 0.042         | 254.7 | 3.27              |
|       |                                | 264.2 | 0.037         | 258.3 | 3.16              |
|       |                                | 267.9 | 0.034         | 261.5 | 2.38              |
|       |                                | 270.5 | 0.034         | 264.2 | 2.01              |
|       |                                | 273.1 | 0.032         | 267.9 | 1.83              |
|       |                                |       |               | 270.5 | 1.49              |
|       |                                |       |               | 273.1 | 1.39              |
| $T/K$ | $I_{rel}(ESR)^b)$              |       |               |       |                   |
| 3.2   | 105.0                          |       |               |       |                   |
| 5.5   | 68.6                           |       |               |       |                   |
| 10.2  | 41.7                           |       |               |       |                   |
| 16.2  | 27.9                           |       |               |       |                   |
| 39.6  | 12.5                           |       |               |       |                   |

<sup>a)</sup> Rate constant of the thermal reaction  $\mathbf{1} \rightarrow \mathbf{2} + N_2$ .

<sup>b)</sup> ESR signal intensities of <sup>3</sup>a (Fig. 3).

<sup>c)</sup> Initial absorbance of transient <sup>3</sup>a measured at 339 nm.

<sup>d)</sup> Lifetime of <sup>3</sup>a in degassed glycerol solution.

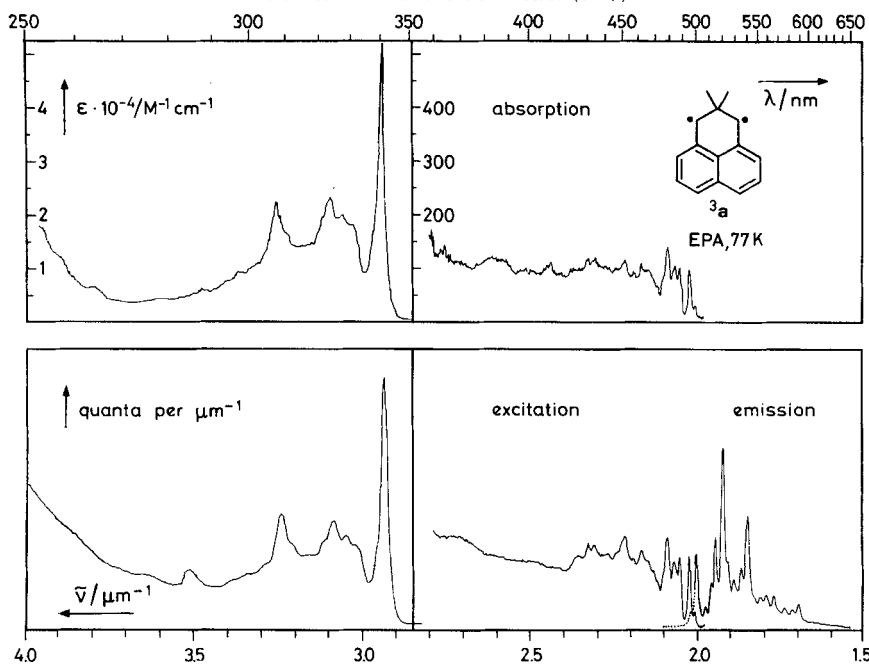


Fig. 1. Absorption, fluorescence emission, and fluorescence excitation spectra of  $^3\mathbf{a}$  in EPA glass at 77 K. The absorption spectrum was recorded at low conversion and was corrected for remaining  $\mathbf{1}$  by deducing *ca.* 95% of the spectrum recorded prior to irradiation, until the sharp 0-0 transition of  $\mathbf{1}$  at 320 nm (Fig. 2) disappeared. The fluorescence spectra are corrected and plotted in arbitrary units of quanta per wavenumber. The extinction coefficients of  $^3\mathbf{a}$  were estimated by reference to those of  $\mathbf{1}$  and the extent of conversion.

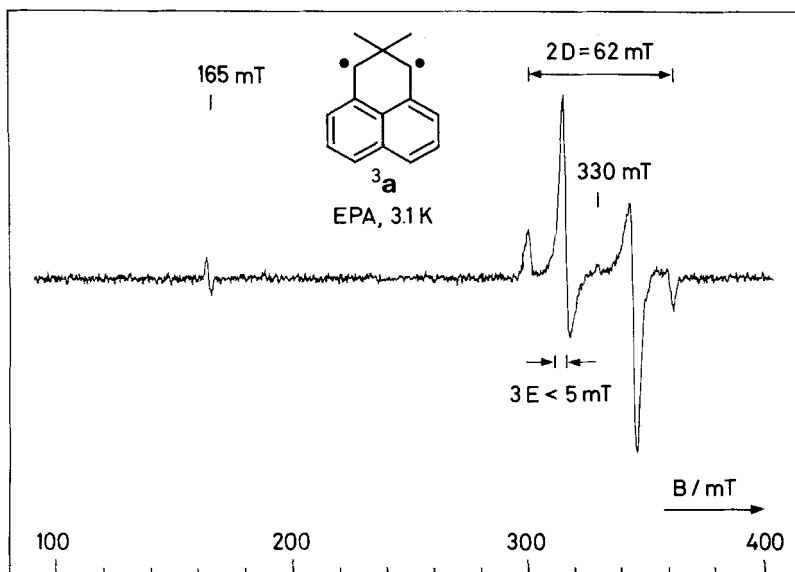


Fig. 2. ESR spectrum of randomly oriented  $^3\mathbf{a}$  in EPA glass at 3.1 K

*Irradiation of 1 and 2 at 77 K; Spectroscopic Identification of the Triplet Biradical <sup>3</sup>a.*

While the hydrocarbon **1** was essentially photostable at room temperature, it was rapidly converted to a photoproduct upon 313 nm irradiation at 77 K in an EPA glass (5 parts Et<sub>2</sub>O, 5 parts isopentane, 2 parts EtOH). A weak absorption band with a series of sharp peaks beginning at 498.5 nm appeared together with a strong band led by a prominent O–O transition at 341 nm. The persistent new compound gave rise to a green, long-lived fluorescence emission ( $\tau_f = 560 \pm 20$  ns, first peak at 499 nm). At small conversions ( $\leq 10\%$ ), the spectral changes could be attributed to the formation of a single new species, since the excitation spectrum of the green fluorescence was in excellent agreement with the new features in the absorption spectrum (Fig. 1). The same species was generated by triplet sensitization of **1** with benzophenone at 77 K (365 nm irradiation of an EPA glass containing  $5 \cdot 10^{-2}$  M of **1**). The photoproduct was quantitatively reconverted to the starting material **1** upon warming and thawing of the glass. No stable photoproducts or loss of **1** was detected except after prolonged irradiation at 77 K.

The close similarity of the optical spectra shown in Fig. 1 with those of the triplet biradicals <sup>3</sup>c [9] and <sup>3</sup>d [10] strongly suggests that the new species is the biradical <sup>3</sup>a. This was verified by measuring the ESR spectrum of a similar sample. A strong signal, characteristic for randomly oriented molecules in a triplet state, was obtained (Fig. 2, zero field parameters  $|D/hc| = 0.033 \pm 0.001$  cm<sup>-1</sup> and  $|E/hc| < 0.002$  cm<sup>-1</sup>; 1 cm<sup>-1</sup> corresponds to 934.8 mT). The dependence of the signal intensity on temperature (Table) is displayed in Fig. 3<sup>1)</sup>. The deviations from the Curie-Weiss law ( $I \cdot T = \text{const.}$ , dotted line) are

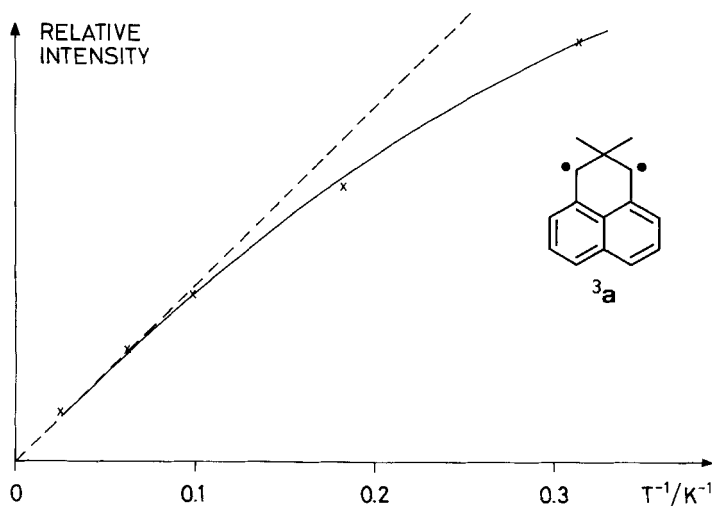


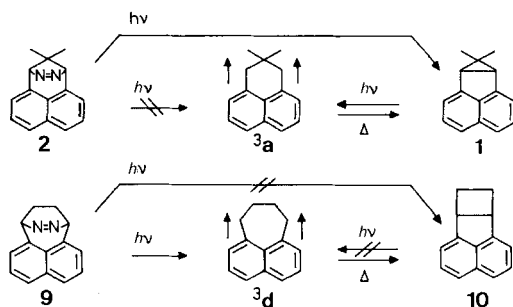
Fig. 3. Temperature dependence of the ESR signal intensity. Explanations are given in the text<sup>2)</sup>.

- <sup>1)</sup> We are most grateful to Dr. H.-P. Meyer, University of Zürich, for hospitality and cooperation.  
<sup>2)</sup> Strictly, these data are consistent either with a triplet ground state,  $E_S - E_T \gg RT$ , or with a very near degeneracy of the lowest singlet and triplet states,  $|E_S - E_T| \ll RT$ . Least-squares fitting of the data to the equation  $I \cdot T = C \cdot \exp(-\Delta E/RT) / [1 + 3 \cdot \exp(-\Delta E/RT)]$ , appropriate for equilibrating singlet and triplet states [21], gave  $E_T - E_S = 0.024$  kJ/mol (solid line, Fig. 3). Similar results have been obtained for **b** [11] **c** and **d** [10]. As pointed out previously [3] [10], it is extremely unlikely that all of these biradicals have  $E_S \cong E_T$  within such narrow limits. Therefore, the second possibility is rejected.

attributed to saturation effects and/or errors in temperature readings at low temperature, *i.e.* we conclude from these data that *the triplet state is the electronic ground state of the biradical a<sup>3</sup>*).

Surprisingly, the azo compound **2** was converted directly to **1** upon 365 nm irradiation in an EPA glass at 77 K. The triplet biradical <sup>3</sup>**a** was not formed (< 0.5%) when light of shorter wavelengths was rigorously excluded in order to avoid the secondary photolysis of the photoproduct **1**. These findings are in sharp contrast with our previous results on the related biradical **d** [10]: photolysis of the corresponding azo precursor **9** gave a near quantitative yield of <sup>3</sup>**d** at 77 K, while the product of ring closure, the naphthocyclobutane **10**, was inert to photolysis at all temperatures (*Scheme 3*).

Scheme 3. Comparison of the Pathways of Formation and Decay of <sup>3</sup>**a** and <sup>3</sup>**d**



*Photophysical Properties of 1 and 2.* In view of the photochemical stability of **1** at room temperature one might have expected that this compound would exhibit the strong fluorescence emission ( $\lambda_{\text{max}} \approx 350$  nm) and triplet-triplet absorption ( $\lambda_{\text{max}} \approx 420$  nm) characteristic of alkylnaphthalene derivatives. In fact, carefully purified samples of **1** emitted virtually no fluorescence at room temperature and no transient intermediate was detected by flash photolysis. The same was true for the azo compound **2**. At 77 K in an EPA glass, however, the fluorescence yield of **1** was quite high,  $\phi_f \approx 0.1$ . The fluorescence lifetime  $\tau_f$  was  $24 \pm 2$  ns and the excitation spectrum agreed well with the absorption spectrum of **1** (*Fig. 4*). For these measurements the intensity of the excitation source had to be kept low to avoid significant conversion to <sup>3</sup>**a**. The low radiative rate constant calculated from these data,  $k_r = \phi/\tau_f \approx 4 \cdot 10^6 \text{ s}^{-1}$ , supports our assignment of the emitting state S<sub>1</sub> to the parity-forbidden <sup>1</sup>L<sub>b</sub> state.

The fluorescence emission of the azo compound **2** remained quite weak when the sample was cooled to 77 K. Two separate emission bands were produced by  $n\pi^*$  excitation (353 nm, azo chromophore) and  $\pi\pi^*$  excitation (265 nm, naphthalene chromophore). With fresh samples the short-wavelength emission ( $\lambda_{\text{max}} \approx 350$  nm) was not due to **1** formed by photolysis, since the spectrum was different and the fluorescence lifetime less than 5 ns. These results are, by themselves, insufficient to establish the dual emission as an authentic property of the bichromophoric molecule **2**. However, such behaviour is not unexpected. A singlet energy transfer from the naphthalene to the azo moiety of **2** by the *Förster* mechanism [22] should be quite inefficient for several reasons: the oscillator strength of the azo chromophore is rather low; the overlap between the naphthalene fluorescence emission and the azo  $n\pi^*$  absorption bands is quite small; the transition moments associated with the two locally excited states are orthogonal to each other in the absence of vibronic interactions. In fact, even the intermolecular fluorescence quenching (no orientational restrictions) of naphthalene by azo compounds is relatively slow and was shown [23] to occur predominantly by the *Dexter* exchange mechanism [24] which requires close contact between the two

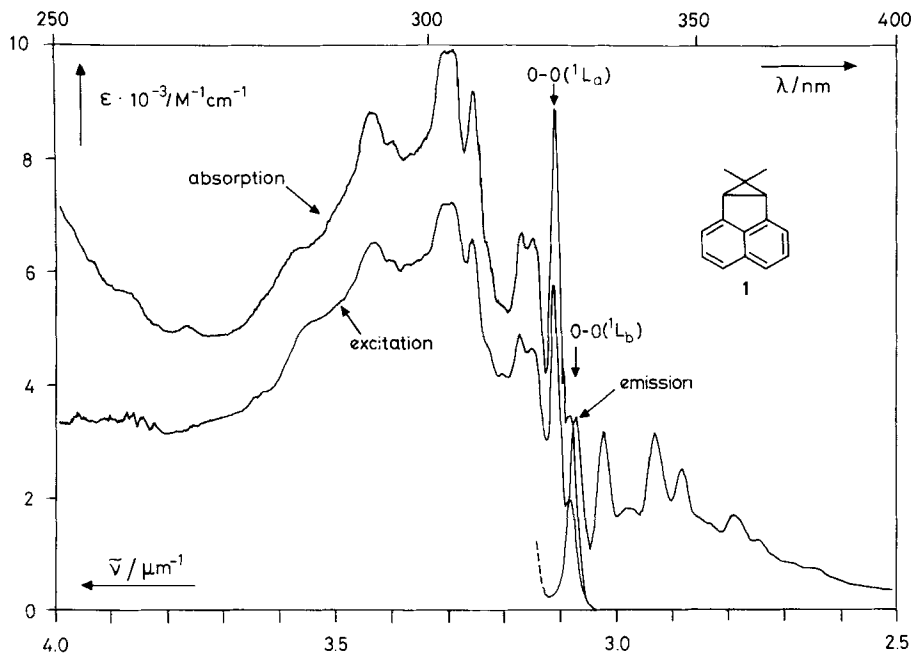


Fig. 4. Absorption, fluorescence emission, and fluorescence excitation spectra of **1** in EPA glass at 77 K. The fluorescence spectra are corrected and plotted in arbitrary units of quanta per wavenumber. The tentative assignments shown for the  ${}^1L_b$  and  ${}^1L_a$  0-0 transitions are based on heuristic arguments (vibrational structure, solvent shifts, and the comparison with the corresponding spectra of the related compounds **7** (R=H) and **10** [15b]).

chromophores. We have found in previous work on the related azo precursor to **b** that  $n\pi^*$  and  $\pi\pi^*$  excitation give rise to entirely different photoreactions [7]. Also, *Cofino et al.* [16b] have reported a highly resolved  $S_2$  fluorescence emission from the azo compound **9**. No long-lived phosphorescence emission was observed from either **1** or **2** at 77 K.

**Mechanism of  ${}^3a$  Formation.** The triplet biradical  ${}^3a$  was readily observed as a transient intermediate with a lifetime of *ca.* 400  $\mu$ s at room temperature after sensitized flash photolysis: the triplet-triplet absorption of benzophenone ( $\lambda_{\max} = 530$  nm), produced by a laser flash at 353 nm, was quenched by both **1** and **2** at a diffusion-controlled rate,  $k_q \cong 6 \cdot 10^9$   $M^{-1}$ , and replaced by the characteristic absorption of  ${}^3a$  (Fig. 1), which was easily identified by its intense and narrow band at 339 nm in benzene solution. At all acceptor concentrations up to  $10^{-2}$  M, the formation of  ${}^3a$  was as fast as the quenching of triplet benzophenone and the triplet states of neither **1** nor **2** could be detected as intermediates. Therefore, the lifetimes of the lowest triplet state of the precursors,  ${}^31^*$  and  ${}^32^*$ , must be less than 100 ns at room temperature. As mentioned above, neither **1** nor **2** gave a detectable amount of  ${}^3a$  upon direct flash photolysis.

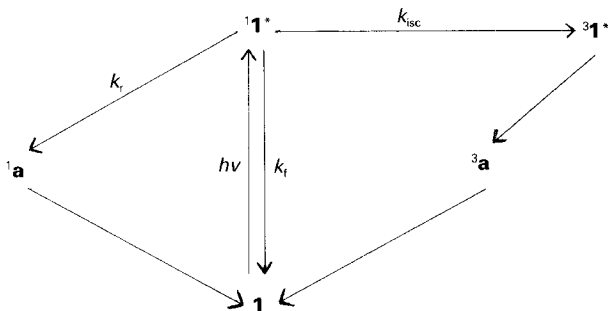
Thus, at room temperature, the sole entry to  ${}^3a$  is provided by triplet sensitization of the precursors. The lowest excited singlet states,  ${}^11^*$  and  ${}^12^*$ , appear to be too short-lived to allow for fluorescence emission or ISC with detectable efficiency. The short lifetime of  ${}^12^*$  is naturally associated with the rapid and efficient expulsion of  $N_2$  yielding **1**. The short lifetime of  ${}^11^*$  must be due to a thermally activated process, since the fluorescence yield of **1** is high at 77 K. Further, the net result of the process must be radiationless conversion to

the ground state, since **1** is photostable at room temperature. We attribute this thermally activated energy wasting to the reaction  ${}^1\mathbf{1}^* \rightarrow {}^1\mathbf{a} \rightarrow \mathbf{1}$  which predominates at room temperature. This interpretation receives strong support from Pagni's observation [14] that the direct irradiation of selectively *exo*-deuterated naphthocyclopropane **7** ( $R=D$ ) induces the rapid epimerization to an *endo/exo*-mixture.

How is the triplet biradical  ${}^3\mathbf{a}$  formed by the direct irradiation of **1** at 77 K? We consider two pathways: ISC from the singlet biradical ( ${}^1\mathbf{1}^* \rightarrow {}^1\mathbf{a} \rightarrow {}^3\mathbf{a}$ ) and ISC from the singlet excited precursor ( ${}^1\mathbf{1}^* \rightarrow {}^3\mathbf{1}^* \rightarrow {}^3\mathbf{a}$ ). Both steps of the first pathway are in fact not expected to be operative in the present case. The first step,  ${}^1\mathbf{1}^* \rightarrow {}^1\mathbf{a}$ , was shown to be limited by a thermal barrier and, according to a quantitative analysis given below, should be quite inefficient at 77 K. A direct entry to  ${}^1\mathbf{a}$  is provided by the photolysis of the azo precursor **2** at 77 K. Since  ${}^3\mathbf{a}$  was not formed under these conditions, the singlet biradical  ${}^1\mathbf{a}$  appears to be too short-lived to undergo ISC (second step). It might be objected that the photoreaction  $\mathbf{2} \rightarrow \mathbf{1}$  does not necessarily proceed *via*  ${}^1\mathbf{a}$  [25], but in any case the first pathway is ruled out by the first argument. The operation of the second pathway can be substantiated as follows: ISC from  ${}^1\mathbf{1}^*$  should, no doubt, be reasonably efficient at 77 K, since the 24 ns lifetime of  ${}^1\mathbf{1}^*$  is unexceptional for a naphthalene derivative; the subsequent reaction  ${}^3\mathbf{1}^* \rightarrow {}^3\mathbf{a}$  is known to proceed at 77 K from the sensitization experiment described above. Notwithstanding, neither phosphorescence nor even a transient triplet-triplet absorption of  ${}^3\mathbf{1}^*$  was observed by flash photolysis at 77 K and  ${}^3\mathbf{a}$  was formed within 100 ns. We conclude that the triplet biradical  ${}^3\mathbf{a}$  is formed by the pathway  ${}^1\mathbf{1}^* \rightarrow {}^3\mathbf{1}^* \rightarrow {}^3\mathbf{a}$  at 77 K and that the adiabatic ring-opening reaction in the triplet state proceeds with a rate exceeding  $10^7 \text{ s}^{-1}$  even at this temperature.

The yield of  ${}^3\mathbf{a}$  upon direct irradiation of **1** should, therefore, increase gradually as the temperature is lowered, *i.e.* as ISC from  ${}^1\mathbf{1}^*$  to  ${}^3\mathbf{1}^*$  becomes competitive with the thermally activated energy-wasting process  ${}^1\mathbf{1}^* \rightarrow {}^1\mathbf{a} \rightarrow \mathbf{1}$ . Indeed, a small amount of  ${}^3\mathbf{a}$  was detected by direct flash photolysis of **1** at temperatures below 0 °C. The addition of *cis*-piperylene up to a concentration of 1M had no influence on the yield of  ${}^3\mathbf{a}$  or on its decay rate. This is not surprising in view of the short lifetime of  ${}^3\mathbf{1}$  even at 77 K. The relative yield of  ${}^3\mathbf{a}$  as a function of temperature was determined from the initial absorbance  $A_0$  at 339 nm immediately after the flash (Table). Taking the yield of  ${}^3\mathbf{a}$  as a measure for the efficiency of ISC from  ${}^1\mathbf{1}^*$ , these data can be analyzed to evaluate the thermal activation energy  $E_a$  of the competing process  ${}^1\mathbf{1}^* \rightarrow {}^1\mathbf{a}$ . Assuming that the rates of fluorescence and ISC,  $k_f$  and  $k_{isc}$ , are essentially independent of temperature, as is usually the case, Scheme 4 leads to

Scheme 4. Mechanistic Scheme for the Quantitative Analysis of  ${}^3\mathbf{a}$  Formation





the linear relationship (Eqn. 1) for the high temperature region where  $k_r(T) \gg k_f + k_{isc}$ .

$$\ln[A_0(T)] \approx \text{Const.} + E_a/RT \quad (1)$$

Least-squares fitting of the data in the Table to the Eqn. 1 gave  $E_a = 15 \pm 1$  kJ/mol for the ring-opening process  $^1\mathbf{1}^* \rightarrow ^1\mathbf{a}$ . This result is fully consistent with the observed temperature dependence of the fluorescence yield of  $\mathbf{1}$ : assuming a normal  $A$  factor of *ca.*  $10^{14}$  s $^{-1}$  for the spin-allowed, monomolecular process  $^1\mathbf{1} \rightarrow ^1\mathbf{a}$ , the calculated rate at 77 K,  $k_r \approx 7 \cdot 10^3$  s $^{-1}$ , is negligible compared with  $k_f + k_{isc} = (\tau_f)^{-1} = 4 \cdot 10^7$  s $^{-1}$ . On the other hand, this process should dominate at room temperature,  $k_r = 2 \cdot 10^{11}$  s $^{-1}$ , thus  $\Phi_f \lesssim 10^{-4}$ .

*Decay Rate of  $^3\mathbf{a}$ : Trapping Experiments.* In degassed, highly fluid solvents, the decay of  $^3\mathbf{a}$  after flash photolysis is initially accelerated by a second-order contribution. To obtain the pure first-order decay rates of  $^3\mathbf{a}$  as a function of temperature, the measurements were done with a more viscous solvent, degassed glycerol, in the temperature range of  $-35$  to  $0^\circ\text{C}$  (Table). Least-squares fitting of these data to an Arrhenius equation gave the parameters  $\log(A/s^{-1}) = 8.4 \pm 0.15$  and  $E_a = 28.6 \pm 0.7$  kJ/mol. Two further rate constants for the decay of  $^3\mathbf{a}$  were measured at much lower temperatures using a solid solution of  $\mathbf{1}$  in polymethylmethacrylate glass,  $k(133 \text{ K}) = 2.8 \cdot 10^{-4}$  s $^{-1}$  and  $k(123 \text{ K}) = 1.0 \cdot 10^{-4}$  s $^{-1}$ . The  $A$  factor is many orders of magnitude lower than usual for monomolecular reactions; this is attributed to the spin barrier which inhibits the process  $^3\mathbf{a} \rightarrow \mathbf{1}$ .

In air-saturated benzene solution at  $20^\circ\text{C}$ , the lifetime of  $^3\mathbf{a}$  was reduced by three orders of magnitude to  $500 \pm 50$  ns. Therefore, virtually all biradicals  $^3\mathbf{a}$  are quenched by oxygen prior to their intrinsic decay to  $\mathbf{1}$ , but the quenching rate is well below the rate of oxygen diffusion. From spin-statistical considerations, we would expect that one in nine encounters between  $^3\mathbf{a}$  and  $^3\text{O}_2$  can yield an oxidation product of  $\mathbf{1}$  by a spin-allowed process. The actual quenching rate  $k_q \approx 1 \cdot 10^9$  M $^{-1}$  s $^{-1}$ , calculated from  $(k_q \cdot \tau)^{-1} \approx [\text{O}_2] = 2 \cdot 10^{-3}$  M in air saturated benzene [26], is significantly lower than 1/9th the rate of diffusion. Thus only every second or third singlet encounter complex  $^1(^3\mathbf{a} \dots ^3\text{O}_2)$  leads to the irreversible destruction of  $^3\mathbf{a}$ .

As expected, the chemical result of  $^3\mathbf{a}$  quenching by oxygen is the formation of oxidation products of  $\mathbf{1}$ . The triplet sensitization of  $\mathbf{1}$  by benzophenone in oxygen-saturated solution led to the rapid disappearance of  $\mathbf{1}^3$ . Chromatographic workup gave acenaphthenone ( $\mathbf{12}$ ) as a main product which, presumably, was formed by secondary sensitized photodecomposition of the primary photooxidation product. The prolonged direct irradiation of  $\mathbf{1}$  at  $-78^\circ\text{C}$  in oxygen-saturated isooctane yielded the cyclic acetal  $\mathbf{13}$  as a main product (Exper. Part). As shown above,  $^3\mathbf{a}$  is formed under these conditions, albeit in low yield; a quantum yield  $\phi(^3\mathbf{a}) \lesssim 4 \cdot 10^{-3}$  is predicted from the analysis of the flash photolysis data by Eqn. 1. Again, the isolated product  $\mathbf{13}$  presumably is formed by secondary photolysis of the primary photooxidation product ( $\mathbf{11}$ , cf. Scheme 1), a reaction with precedent [27]<sup>4</sup>.

Is it possible to intercept the singlet biradical  $^1\mathbf{a}$  with oxygen, i.e. to promote oxygen-catalyzed ISC to  $^3\mathbf{a}$  and the subsequent oxidation of the latter? Several entries to  $^1\mathbf{a}$  were

<sup>3</sup>) A concentration of  $\mathbf{1}$  exceeding  $10^{-2}$  M is necessary to ensure efficient energy transfer prior to the quenching of triplet benzophenone by oxygen.

<sup>4</sup>) We are grateful to Prof. R. M. Wilson, University of Cincinnati, Ohio, for calling our attention to some related cases.

available to test this possibility. We have shown above that the direct irradiation of **1** and, presumably, **2** at room temperature yields <sup>1</sup>**a** with unit quantum efficiency. Both of these photoreactions were not affected by the presence of oxygen up to 1 atm and spot tests to detect traces of peroxides [28] were negative. Further, when the thermal elimination of nitrogen from **2** was carried out under an oxygen pressure of 40 atm, **1** was still the sole product and no traces of peroxides were detected. Finally, **1** was recovered unchanged from a solution in CCl<sub>4</sub> which had been kept at 130 °C for 40 h under 70 atm of oxygen. Under these conditions each molecule **1** has undergone many ring inversions *via* an intermediate or transition state of structure <sup>1</sup>**a**<sup>5</sup>). Assuming that the exothermic, spin-allowed process <sup>1</sup>**a** + <sup>3</sup>O<sub>2</sub> → <sup>3</sup>**a** + <sup>3</sup>O<sub>2</sub> should occur at a diffusion-controlled rate, the complete absence of oxidation products in all these experiments allows us to estimate an upper limit of 1 ps for the lifetime of <sup>1</sup>**a** at room temperature.

All attempts to trap either <sup>1</sup>**a** or <sup>3</sup>**a** by monomolecular addition to acrylonitrile have failed. The formation of <sup>3</sup>**a** in neat acrylonitrile initiated the polymerization of the solvent, whereas several approaches to trap <sup>1</sup>**a** have failed entirely.

**Concluding Remarks.** – The pathways for the formation of the biradical 2,2-dimethyl-1,3-perinaphthadiyl (**a**) from two precursor compounds and the decay of **a** to stable products (*Scheme 1*) have been traced in considerable detail. The C–C bond cleavage of the perinaphtho-fused cyclopropane **1** to form the biradical **a** is a very facile process after electronic excitation; the activation energy amounts to *ca.* 15 kJ/mol in the lowest singlet state <sup>1</sup>**1**\* and less than 10 kJ/mol in the lowest triplet state <sup>3</sup>**1**\*. At room temperature, there is no efficient pathway for ISC from the singlet to the triplet manifold at any stage of the reaction. At low temperatures, ISC from <sup>1</sup>**1**\* to <sup>3</sup>**1**\* provides an entry to the triplet manifold. The triplet ground state of the biradical, <sup>3</sup>**a**, was characterized by several spectroscopic methods and its reactivity in fluid solution was monitored by kinetic flash photolysis and chemical trapping with oxygen. Various indirect approaches have consistently led to the conclusion that the lowest singlet state of the biradical is very short-lived, τ(<sup>1</sup>**a**, 300 K) < 1 ps.

Biradical intermediates are of considerable interest as bifunctional reactants with the potential to form two new bonds with a suitable reagent. Triplet biradicals can be fairly long-lived, *e.g.* τ(<sup>3</sup>**a**, 300 K) = 400 μs, due to the spin barrier which inhibits the intramolecular rearrangement to stable products. For the same reason, triplet biradicals are unfortunately rather reluctant to undergo intermolecular reactions, except with open-shell reagents such as oxygen. The lifetime of the singlet biradical <sup>1</sup>**a** appears to be insufficient to allow for ISC to <sup>3</sup>**a** or for intermolecular trapping. Flash photolysis and trapping studies of the related biradicals **d** [10b] and **e** [15b] are in progress. It turns out that subtle changes in structure can have a profound influence on the lifetimes and ISC efficiencies of these conjugated biradicals and thus give rise to unexcepted differences in the chemical reactivity of closely related compounds (*cf., e.g., Scheme 3*).

<sup>5</sup>) Although we have not been able to determine the rate of ring inversion for **1**, the known [5] rate constant for the parent naphthocyclopropane **7** may be taken as a lower limit, since **1** is destabilized by steric interaction between the aromatic ring and the *endo*-CH<sub>3</sub> group, and <sup>1</sup>**a** should, if anything, be stabilized by hyperconjugation through the dimethylmethylene bridge. The ring inversion in the bis(dimethylcyclopropane)precursor to <sup>1</sup>**e** is indeed much faster than in **7** [15], though this rate enhancement may also be attributed to the additional stabilization of <sup>1</sup>**e** by the second cyclopropane ring.

**Experimental.** – *Kinetic and Spectrographic Flash Photolysis.* A conventional electrical discharge was used as an excitation source for long-lived transients ( $\tau > 50 \mu\text{s}$ ), and frequency-tripled (353 nm) or quadrupled (265 nm) pulses from a Nd glass laser for short-lived transients ( $10 \text{ ns} < \tau < 100 \mu\text{s}$ ). The detection system allowed for the simultaneous capture of the kinetics (at a given wavelength) and the transient spectrum (at a given time delay after excitation) in digital form with ns time resolution. Details of the experimental setup have been given in [3].

*Fluorescence Spectra and Fluorescence Lifetimes.* Corrected fluorescence emission and excitation spectra were recorded on a Spex Fluorolog 2 (model 111 C); for phosphorescence measurements a pulsed lamp accessory (model 1934 C) was available. Fluorescence lifetimes ( $\tau > 10 \text{ ns}$ ) were measured with the laser flash photolysis setup with the aid of a pulse chopper.

*Absorption spectra* are quoted as  $\lambda_{\text{max}}/\text{nm}$  ( $\log \epsilon / \text{M}^{-1} \text{ cm}^{-1}$ ) and were recorded on a Beckman UV 5240 which was equipped with a thermostated quartz dewar for low-temperature spectra down to 77 K.

*2,2-Dimethyl-2,3-dihydrophenalene-1,3-diol (c-4 and t-4), 2,2-Dimethyl-2,3-dihydrophenalene-1,3-dione (3; 1 g, 4.5 mmol)* [17] [18] was reduced by catalytic hydrogenation with platinum oxide in abs. EtOH ( $20 \text{ cm}^3$ ) at ambient temp. and pressure. When the  $\text{H}_2$  uptake ceased, the mixture was treated with a small amount of charcoal, filtered, and evaporated to dryness. Slow crystallization from toluene gave 0.8 g of colorless **c-4**, m.p. 177–8°. The mother liquor containing a small amount of **t-4** (ca. 0.1 g) was purified by column chromatography on silica with  $\text{CH}_2\text{Cl}_2/\text{AcOEt}$  4:1 (**c-4**:  $R_f$  0.38; **t-4**:  $R_f$  0.46). UV (EtOH): **c-4**: 318 sh (2.40), 313 (2.76), 295 (3.74), 285 (3.87), 275 (3.80).  $^1\text{H-NMR}$  ( $\text{CD}_3\text{COCD}_3$ , 60 MHz): **c-4**: 0.86 (s, 3H); 1.19 (s, 3H); 3.0 (br. s, 2H (–OH)); 4.72 (br. s, 2H); 7.3–7.9 (m, 6H); **t-4**: 0.99 (s, 6H); 3.0 (br. s, 2H (–OH)); 4.82 (br. s, 2H); 7.3–8.0 (m, 6H). MS: **c-4**: 228 (100,  $M^+$ ), 211 (45), 195 (84), 182 (42), 168 (76), 152 (25).

*1,3-Dibromo-2,2-dimethyl-2,3-dihydrophenalene (c-5 and t-5).* A soln. of the diol **c-4** (0.34 g, 1.5 mmol) in dry  $\text{CH}_2\text{Cl}_2$  ( $25 \text{ cm}^3$ , dist. from  $\text{P}_2\text{O}_5$ ) was added dropwise under inert gas to a stirred soln. of freshly distilled  $\text{PBr}_3$  (0.49 g, 1.8 mmol) in dry  $\text{CH}_2\text{Cl}_2$  ( $10 \text{ cm}^3$ ) which was kept at  $-10$  to  $-15^\circ$ . The mixture was then kept at  $0^\circ$  for 5 h, quenched with ice, and extracted with dilute, cold bicarbonate. The org. layer was dried and the solvent evaporated. The oily residue was dissolved in a small amount of  $\text{Et}_2\text{O}$  and diluted with petrol ether. Slow crystallization upon cooling gave 0.17 g colorless crystals of **c-5**, m.p.  $108^\circ$ . Further cooling yielded 0.23 g of a mixture of **c-5** and **t-5** (combined yield 75%). For analytical purposes the *trans*-isomer was isolated by column chromatography with AcOEt on silica (**c-5**:  $R_f$  0.65; **t-5**:  $R_f$  0.53). UV (hexane): **c-5**: 308 sh (3.71), 296 (3.85), 287 sh (3.79).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 60 MHz): **c-5**: 0.86 (s, 3H); 1.53 (s, 3H); 5.52 (s, 2H); 7.3–7.9 (m, 6H).  $^1\text{H-NMR}$  ( $\text{CD}_3\text{COCD}_3$ , 90 MHz,  $-20^\circ$ ): **t-5**: 0.99 (s, 3H); 1.56 (s, 3H); 5.95 (s, 1H); 6.05 (s, 1H); 7.4–8.1 (m, 6H). MS: **c-5**: 356 (10,  $M^+$  + 2), 354 (17,  $M^+$ ), 352 (10,  $M^+$  – 2), 275 (62), 273 (60), 194 (66), 179 (100).

*7,7-Dimethyl-6b,7a-dihydro-7H-cycloprop[*a*]acenaphthylene (1).* A degassed soln. of the dibromide (**c-5** or isomeric mixture **c-5** + **t-5**, 0.4 g, 1.13 mmol) in dry benzene ( $60 \text{ cm}^3$ ) was agitated over amalgamated Li (1% Li [29]) for 3 h. The soln. was decanted, filtered, evaporated, and chromatographed with cyclohexane on silica ( $R_f$  [29]) for 3 h. The soln. was decanted, filtered, evaporated, and chromatographed with cyclohexane on silica ( $R_f$  0.3). Sublimation at  $35^\circ/1 \text{ Pa}$  gave 85 mg (39%) of **1** as a crystalline solid, m.p.  $62\text{--}3^\circ$ . UV (hexane) 318 sh (3.53), 312 (3.75), 304 sh (3.81), 299 (3.94), 287 (3.85), 227 (4.71).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 0.39 (s, 3H); 1.31 (s, 3H); 2.85 (s, 2H); 7.2–7.6 (m, 6H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , H-dec. (rel. int.)): 14.7 (93); 27.5 (109); 33.3 (73); 38.1 (240); 120.5 (206); 122.6 (201); 127.3 (205); 131.0 (51); 139.6 (44); 143.5 (117). MS: 194 (21,  $M^+$ ), 180 (28), 179 (100), 178 (32).

*1,4-Dihydro-1,4-isopropylidenenaphtho[1,8-de][1,2]-diazepine (2).* Di-(*tert*-butyl)hydrazodiformate (*Al-drich*, 72 mg, 0.31 mmol) was added to a soln. of **K** (27 mg, 0.62 mmol) in dry *t*-BuOH ( $3 \text{ cm}^3$ ) and evaporated to dryness [30]. The residue was suspended in dry DMF ( $3 \text{ cm}^3$ ) and added to a soln. of **c-5** (110 mg, 0.31 mmol) in dry DMF ( $2 \text{ cm}^3$ ). The mixture was stirred for 20 h at ambient temp., quenched with ice/ $\text{H}_2\text{O}$  ( $30 \text{ cm}^3$ ), and extracted four times with a total of  $20 \text{ cm}^3$   $\text{Et}_2\text{O}$ . The  $\text{Et}_2\text{O}$  extracts were dried, evaporated, and the residue chromatographed with  $\text{CHCl}_3$  on silica. The product **6** was obtained as the second, main fraction (90 mg, 66%;  $R_f$  0.37).

A soln. of **6** (90 mg) in  $\text{CCl}_4$  was saturated with gaseous HCl (10 min) and the resulting suspension stirred overnight. The precipitate was filtered, washed with  $\text{CCl}_4$ , dissolved in  $\text{H}_2\text{O}$ , and neutralized with bicarbonate. The mixture was extracted with  $\text{CH}_2\text{Cl}_2$  and treated dropwise with a conc. soln. of *N*-phenyl-1,2,4-triazoline-3,5-dione (*Fluka*) in  $\text{CH}_2\text{Cl}_2$ , until the mixture was no longer discolored immediately [7]. The azo compound **2** (ca. 6 mg) was purified by prep. TLC on silica with  $\text{CHCl}_3$  ( $R_f$  0.39). UV ( $\text{CH}_2\text{Cl}_2$ ;  $\log \epsilon$  determined by reference to the decomposition product **1**): 377 (3.46), 365 sh (3.25), 296 (4.03), 284 (3.92), 274 sh (3.72).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ): 0.82 (s, 3H); 1.13 (s, 3H); 5.53 (s, 2H); 7.3–7.9 (m, 6H).

*4,4-Dimethyl-2,5-(1',8'-naphthylene)-1,3-dioxolane (13).* A soln. of **1** (4 mg) in iso-octane (10 ml) was kept at  $-78^\circ$ , saturated with bubbling oxygen, and irradiated with 313 nm light (filtered from a 200 W high-pressure Hg arc) until 80% of the starting material had disappeared (18 h). The soln. was evaporated and the residue chromatographed with  $\text{CHCl}_3$  on silica. The acetal **13** was eluted as the main product (ca. 2 to 3 mg,  $R_f = 0.33$ ).

<sup>1</sup>H-NMR (CHCl<sub>3</sub>, 90 MHz): 0.88 (s, 3H); 1.2–1.4 (m, impurities, < 1H); 1.55 (s, 3H); 5.09 (s, 1H); 6.29 (s, 1H); 7.2–7.8 (m, 6H). MS: 226 (6, M<sup>+</sup>), 169 (16), 168 (100), 149 (17), 140 (23), 139 (19).

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