no exchange with $\mathbf{1}^{-}\cdot$ or $\cdot\mathbf{1}^{2-}\cdot$ since the high-field lines of the new pentet were clearly resolved from the high-field lines of the spectra of Figure 1a and 1b. Finally the spectrum of $\mathbf{1}^{-}\cdot$ and $\cdot\mathbf{1}^{2-}\cdot$ disappeared completely to yield the pentet of Figure 1c (a^H = 1.26 G in MeCN, a^H = 1.30 G in Me_2SO, g = 2.00495 in Me_2SO) which we assign to $\mathbf{1}^{3-}\cdot$. Occasionally an additional partially resolved triplet or pentet splitting of ~0.05 G was observed. Upon standing, the pentent of Figure 1c slowly reverted to the high-g pentet and/or triplet, which upon further electroreduction regenerated the spectra of Figure 1c. Addition of **1** converted the spectrum of Figure 1c to the spectra of Figure 1a and/or 1b. Treatment of solutions giving the spectrum of Figure 1c with oxygen immediately converted the spectrum to a doublet of doublets (a^H = 2.00, 2.35 G; g = 2.0050), which we believe is a semiquinone radical di- to trianion in which one ring has been substituted by OH or OR.

For $\mathbf{1}^{3-}\cdot$, the second and fourth peaks display selective line broadening at 25 °C. Cooling MeCN solutions yielded a ~1:4:1 triplet of sharp wing and center peaks at ~−20 °C, while heating caused the pentet to approach an intensity ratio of 1:4:6:4:1. From the line broadening, $\Delta H^{\ddagger}$ for electron jump was calculated to be 3.7 kcal/mol ($\Delta S^{\ddagger}$ = −24.3 eu). The spectrum of Figure 1c was also produced by the reduction of **1** with Me_3COK in MeCN in the presence of [2.2.2]cryptand or 18-crown-6 ether. The cryptand or crown ether greatly increased the reducing ability of Me_3COK in MeCN, and in fact the addition of the cryptand of crown ether to Me_3COK solutions yielding the spectra of Figure 1a or 1b converted the spectra to that of Figure 1c.[7] Under these conditions the spectra often were a mixture of the three line pattern (high g) assigned to $\cdot\mathbf{1}^{2-}\cdot$ and the low-g pentet of $\mathbf{1}^{3-}\cdot$. Ion pairing did not appear to have any effect upon the observed spectra, since the low-g pentet was observed with either a deficiency or an excess of the cryptand or crown ether.[8]

The energy barrier for electron migration between the quinone rings is lower for $\mathbf{1}^{3-}\cdot$ than for $\mathbf{1}^{1-}\cdot$, but $\Delta S^{\ddagger}$ greatly favors the electron migration of $\mathbf{1}\cdot^{-}$. This may be connected with more extensive solvation for $\mathbf{1}^{3-}\cdot$ than for $\mathbf{1}^{-}\cdot$. The normal Arrhenius behavior of both radical anions gives no evidence that electron tunneling is involved in the process which time averages the quinone rings.

Radical Anions of Triptycene Tris(quinone). Reduction of **2** at 25 °C in Me_2SO or MeCN at a Hg pool or Pt ($Bu_4N^+ClO_4^-$) also gave a number of discrete paramagnetic states, one of which is apparently the triradical trianion. The initially observed spectrum is a seven line pattern (in Me_2SO, a^H = 0.66 G (6 H), g = 2.00507) which is undoubtedly $\mathbf{2}^{-}\cdot$. Reduction of **2** by KI in Me_2SO in the presence of Hg or by traces of Me_3COK in Me_2SO, MeCN, or DMF also yielded $\mathbf{2}^{-}\cdot$. Selective line broadening was not observed at −90° C in DMF.

Reduction of **2** at higher potentials yielded a 1:2:1 triplet [a^H = 2.60 G (2 H)] which could also be observed by reaction with Me_3COK in Me_2SO. By analogy to the reduction products of **1**, this ESR spectrum is assigned to the triradical trianion in which there is no exchange of the electrons.[4] There was no indication of a discrete species which could be identified as the diradical dianion, possibly because $\cdot\mathbf{2}^{2-}\cdot$ has a heptet ESR spectrum indistinguishable from $\mathbf{2}^{-}\cdot$.[7] The spectra asssigned to $\mathbf{2}^{-}\cdot$ and $\cdot\dot{\mathbf{2}}^{3-}\cdot$ were not immediately destroyed upon exposure to oxygen.

At still higher reduction potentials at a Hg pool, a second heptet is produced [α^H = 0.68 G (6 H)] which is not time averaged with the triplet that precedes it. This species is quite reactive and cannot be observed in the absence of electrolysis. This heptet may be $\dot{\mathbf{2}}^{4-}\cdot$ or $\dot{\mathbf{2}}^{5-}\cdot$. In the triptycene tris(quinone) system intramolecular electron transfer between the quinone rings occurs more readily than for the bis(quinone), and the possibility of a completely delocalized system for $\mathbf{2}^{-}\cdot$ and $\mathbf{2}^{5-}\cdot$ exists.[9]

Triptycene tris(quinone) was synthesized in three steps from 1,4,5,8-tetraacetoxyanthracene[10] (**3**) and benzoquinone. The adduct **4** was prepated in 93% yield by refluxing **3** (18.7 g, 45.6 mmol) with benzoquinone (5.40 g, 50.2 mmol) in xylene (200 mL) for 20 h: mp 244–248 °C from 1,2-dichloroethane; ^{1}H NMR ($CDCl_3$) δ 6.95 (2 H), 6.85 (2 H), 6.45 (2 H), 5.1 (2 H), 3.15 (2 H), 2.45 (6 H), and 2.40 (6 H). Anal. Calcd for $C_{28}H_{22}O_{10}$: C, 64.9; H, 4.23. Found: C, 64.6; H, 4.63.

The adduct **4** (0.55 g, 1.06 mmol) was hydrolyzed and rearranged to 1,4,5,8,13,16-hexahydroxytriptycene (**5**) by treatment with KOH (0.5 g) in 10 mL of water and 10 mL of acetonitrile (25 °C, 2 h) under nitrogen. Acidification with dilute H_2SO_4 gave **5** (0.29 g, 65%). A sample for analysis was precipitated from Me_2SO with benzene. Anal. Calcd for $C_{20}H_{14}O_6\cdot 4H_2O$: C, 56.8; H, 5.2. Found: C, 56.5; H, 5.3; ^{1}H NMR (Me_2SO-d_6) δ 6.2 (2 H) and 6.1 (6 H).

The hexaacetyl derivative of **5**, recrystallized from acetic acid, melted at 340 °C. Anal. Calcd for $C_{32}H_{26}O_{12}$: C, 63.8; H, 4.35. Found: C, 63.7; H, 4.42. IR (KBr) 1770, 1490, 1370, 1200, 1170, 1060, and 900 cm^{-1}.

The tris(hydroquinone) (**5**) (10.0 g, 28.5 mmol) was stirred with $Na_2Cr_2O_7\cdot 2H_2O$ (8.52 g, 28.5 mmol) in 1 L of acetic acid at 25 °C for 1 h. On dilution with 1 L of water, **2** (8.8 g, 90%) precipitated (mp >330 °C) from 1,2-dichloroethane. ^{1}H NMR (Me_2SO-d_6) δ 6.1 (6 H), and 5.7 (2 H); UV (CH_2Cl_2) λ_{max} (ϵ) 242 (3444) and 342 nm (78). Anal. Calcd for $C_{20}H_8O_6$: C, 69.8; H, 2.34. Found: C, 69.4; H, 2.60.

(7) Treatment of the monohydroquinone derivative of **1** with $KOCMe_3$ in Me_2SO initially forms a mixture of $\mathbf{1}^{3-}\cdot$ and $\cdot\mathbf{1}^{2-}\cdot$ with the percentage of $\cdot\mathbf{1}^{2-}\cdot$ increasing with the amount of base employed. Addition of [2.2.2]-cryptand to these solutions results in an excellent spectrum of $\mathbf{1}^{3-}\cdot$ containing only a trace of $\cdot\mathbf{1}^{2-}\cdot$. In solution the monohydroquinone is known to disproportionate to **1** and the bis(hydroquinone).[2]

(8) Addition of *tert*-butyl alcohol or water to solutions of $\mathbf{1}^{3-}\cdot$ generated by $KOCMe_3$/[2.2.2]-cryptand increases the proportion of $\cdot\mathbf{1}^{2-}\cdot$ present and with sufficient water will convert the spectrum completely to $\cdot\mathbf{1}^{2-}\cdot$. There is no evidence of time averaging between the two species as would be expected if they were protonated and deprotonated forms of the same reduction state. The effect of proton donors apparently involves the equilibrium, $2\mathbf{1}^{3-}\cdot \rightleftharpoons \cdot\mathbf{1}^{2-}\cdot + \mathbf{1}^{4-}$, which is shifted to the right by preferential protonation of $\mathbf{1}^{4-}$.

(9) The rate of triplet exiton transfer in triptycene is $>10^{10}$ s^{-1} at 77 K. At 20 K the triplet exiton in tribenzotriptycene is localized mainly in one naphthtalene ring (de Groot, M. S.; Van der Walls, J. M. *Mol. Phys.* **1963**, 545).

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Anthracyclines and Related Substances. 3. Regiospecific Total Synthesis of 11-Deoxydaunomycinone

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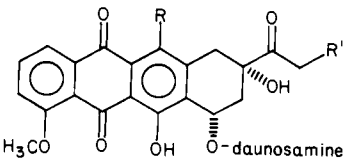
The antitumor drugs adriamycin[1] (**1a**) and daunomycin[2] (**1b**) have enjoyed widespread use in the treatment of neoplastic conditions due to their relatively broad spectrum of antitumor activity.[3]



1a, R = R′ = OH
b, R = OH; R′ = H
2a, R = H; R′ = OH
b, R = R′ = H

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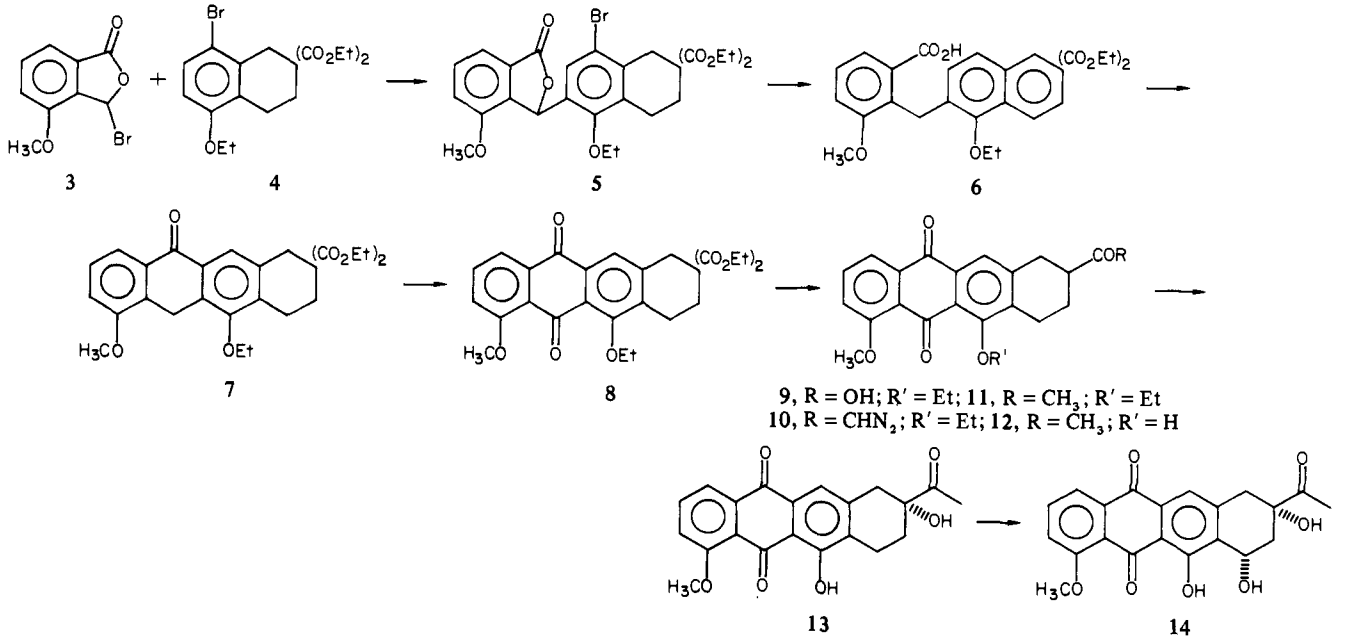
Scheme I



However, these drugs have an associated irreversible cardiomyopathy[4] which limits their effectiveness. Studies of analogues of adriamycin and daunomycin have led to the discovery of a few compounds in this class with a better therapeutic index.[5] Recently Arcamone et al.[6] announced the isolation of a series of 11-deoxyanthracyclines, amongst which were **2a** and **2b**. The report that the former compound had a somewhat better therapeutic index than **1a** (although at a higher dose level) prompted us to attempt total synthesis in this series. We now report success in the synthesis of 11-deoxydaunomycinone (**14**), the aglycon of **2b**.

Our approach to **14** involves a variation of the general route that we have developed to the anthracycline skeleton[7] and is based on a convergent AB + D → ABD → ABCD pattern. The key step in controlling regiochemistry utilizes the Friedel–Crafts alkylation ($SnCl_4/CH_2Cl_2$/25 °C/24 h) of tetralin **4**[8] by the previously described[7] bromolactone **3** (Scheme I). This gives the intermediate[9] phthalidotetralin[10a] **5** in 86% yield as white needles, mp 126 °C; NMR[10b] δ 1.24 (t, 6 H, *J* = 7.0 Hz), 1.41 (t, 3 H, *J* = 6.9 Hz), 2.26 (t, 2 H, *J* = 6.9 Hz), 2.85 (t, 2 H, *J* = 7.1), 3.21 (s, 2 H), 3.73 (s, 3 H), 3.96 (q, 2 H, *J* = 6.9 Hz), 4.20 (q, 4 H, *J* = 7.0 Hz), 6.69 (s, 1 H), 6.77 (s, 1 H), 7.10–7.58 (m, 3 H); IR (Nujol) 1755, 1735.

Catalytic reduction (Pd–C/HOAc/85 °C) of **5** then provided the acid **6** (91%) as white needles, mp 119–120 °C; NMR (acetone) δ 1.24 (t, 6 H, *J* = 7.0 Hz), 1.46 (t, 3 H, *J* = 7.0 Hz), 2.31 (t, 2 H, *J* = 7.0 Hz), 2.88 (t, 2 H, *J* = 7.0 Hz), 3.19 (s, 2 H), 3.78 (s, 3 H), 4.00 (q, 2 H, *J* = 7.0 Hz), 4.20 (q, 4 H, *J* = 7.0 Hz), 4.48 (s, 2 H), 6.40 (d, 1 H, *J* = 8.0 Hz), 6.70 (d, 1 H, *J* = 8.0 Hz), 7.06–7.50 (m, 3 H); IR (Nujol) 1745, 1725, 1680. Cyclization of **6** ($CF_3CO_2H/(CF_3CO)_2O$/25 °C/1 h) afforded **7** solely as the anthrone (81%), yellow-green needles, mp 130 °C; IR (Nujol) 1735, 1600; NMR δ 4.09 (s, 2 H); no anthranol being detectable spectroscopically. Oxidation (Jones reagent/acetone/25 °C/2 h) of **7** to the tetrahydronaphthacenequinone **8** (97%) gave yellow needles, mp 127–128 °C; NMR δ 1.23 (t, 6 H, *J* = 7.1 Hz), 1.47 (t, 3 H, *J* = 7.0 Hz), 2.33 (t, 2 H, *J* = 6.4 Hz), 2.92 (t, 2 H, *J* = 6.5 Hz), 3.35 (s, 2 H), 3.99 (s, 3 H), 4.18 (q, 6 H, *J* = 7.0 Hz), 7.25–7.96 (m, 4 H). IR (Nujol) 1730, 1675. Hydrolysis (NaOH/EtOH/reflux/16 h) and subsequent decarboxylation (HOAc/piperidine/reflux/3 h) of **8** led to the monoacid **9** (86%) as yellow needles, mp 249–250 °C; NMR δ 1.49 (t, 3 H, *J* = 7.0 Hz), 1.73–2.24 (m, 3 H), 2.78–3.20 (m, 4 H), 4.00 (s, 3 H), 4.10 (q, 2 H, *J* = 6.9 Hz), 7.33–7.91 (m, 4 H); IR (Nujol) 1720–1675 (br).

The crude acid chloride prepared ($SOCl_2$/catalytic DMF) from **9** was treated with diazomethane (16 equiv/0 °C) in ether to give the diazo ketone **10** as a yellow crystalline compound [mp 134–136 °C (evolution of nitrogen); NMR δ 5.41 (s, 1 H); IR (Nujol) 2090, 1670, 1625)] which on reduction[11] by hydrogen iodide then provided a 77% overall yield (based on acid **9**) of methyl ketone **11** as yellow needles, mp 172 °C; NMR δ 1.49 (t, 3 H, *J* = 7.0 Hz), 1.84 (m, 1 H), 2.26 (s, 3 H), 2.16–2.34 (m, 1 H), 2.71–3.08 (m, 5 H), 3.99 (s, 3 H), 4.08 (q, 2 H, *J* = 7.0 Hz), 7.22–7.88 (m, 4 H); IR (Nujol) 1710, 1675. Selective deethylation ($AlCl_3$/$PhNO_2$/70 °C/3 h)[12] of **11** followed by recrystallization then afforded the phenol **12** (90%) as orange blades, mp 223–6 °C; NMR δ 1.81 (s, 2 H), 2.27 (s, 3 H), 2.27 (m, 1 H), 2.97–3.02 (m, 4 H), 4.06 (s, 3 H), 7.26–8.01 (m, 4 H), 13.37 (s, 1 H); IR ($CDCl_3$) (Nujol) 1705, 1685. Hydroxylation at C-9 was accomplished[13] by a standard oxidation (*t*-BuOK/O_2/$(EtO)_3P$/DMF/−30 °C/20 min) to give the tertiary α-hydroxy ketone **13** (77%, 87% based on recovered **12**) again as orange blades, mp 209–211 °C; NMR δ 2.01 (m, 2 H), 2.36 (s, 3 H), 2.75 (d, 1 H), *J* = 17.6 Hz), 3.06–3.15 (m, 2 H), 3.31 (d, 1 H, *J* = 17.4 Hz), 3.65 (s, 1 H), 4.07 (s, 3 H), 7.26–8.00 (m, 4 H), 13.37 (s, 1 H); IR ($CDCl_3$) (Nujol) 3470, 1715, 1685, 1630.

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(9) This intermediate can be used for synthesis in the daunomycinone series as will be reported later.
(10) (a) All compounds gave satisfactory spectroscopic data and elemental analyses. (b) All NMR spectra were taken in deuteriochloroform solution unless otherwise indicated.
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The most satisfactory approach to the introduction of the required C-7 hydroxyl group involved a three-step sequence.[14] Ketalization (ethylene glycol, PhH, TsOH, 80 °C) of **13** afforded the C-13 ketal [mp 258–260 °C; IR ($CDCl_3$) (Nujol) 1665, 1625, 1095, 1015] in quantitative yield, which when hydroxylated (1.3 equiv of Br_2/AIBN/CCl_4–$CHCl_3$–H_2O/70 °C) led to a 2:1 mixture (the desired isomer predominating) of the epimeric C-7 alcohols (65%), mp 95–100 °C; NMR δ 1.42 (s, 3 H), 4.06 (s, 7 H), 5.29, 5.84 (s, 1 H), 7.17–8.07 (m, 4 H), 13.61, 13.75 (s, 1 H); IR ($CDCl_3$) (Nujol) 3675, 1675, 1630; MS *m/e* 426 (M^+), 321, 87. Subsequent deketalization (80% CF_3CO_2H/0 °C) of this mixture then gave quantitatively racemic **14**, mp 210–213 °C, NMR δ 2.41 ($COCH_3$), 4.08 (OCH_3), 7.18–8.00 (ArH), 13.66 (ArOH); MS *m/e* 382 (M^+), 321, 293, 44, 43; UV (max) (MeOH) 415, 258, 228 mm; TLC R_f = 0.3 (silica) in CH_3OH:CH_2Cl_2::1:20. This material proved to be identical in all of these characteristics with a sample of the natural product[15] having mp 210–213 °C, mmp 210–213 °C.

The application of the above approach to related anthracyclinones is being investigated.

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Photochemistry of a 1,1-Diazene, *N*-(2,2,5,5-Tetramethylpyrrolidinyl)nitrene

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The photochemistry of the 1,1-diazene has never been examined due to its transient nature. Several theoretical groups have calculated the order of the electronic states of the 1,1-diazene (aminonitrene, *N*-nitrene) during the past decade.[1,2] Goddard's GVB–CI calculations of the parent H_2N–N suggest a ground-state singlet with low-lying n,π^* singlet (50.7 kcal) and triplet states (13.8 kcal) (Figure 1).[1f] The 1,1-diazene is isoelectronic with the carbonyl, a functional group whose photochemistry is well documented. The recent synthesis and characterization of persistent 1,1-diazenes[3] allows an investigation of the photochemical reactivity of this species. We report the direct and sensitized irradiation of N-(2,2,5,5-tetramethylpyrrolidinyl)nitrene **1** in the visible region (n,π^* transition) which reveal both unimolecular and bimolecular photoreactivity. In addition, the fluorescence spectrum of a 1,1-diazene has been obtained.

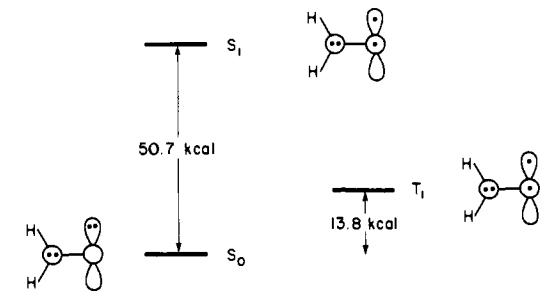

Figure 1.

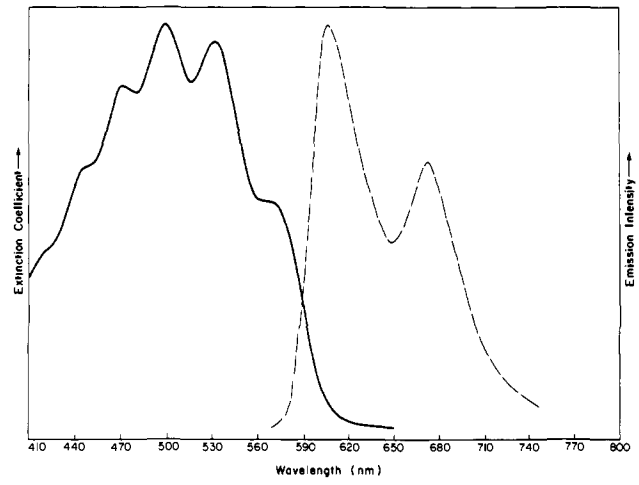

Figure 2. Absorption spectrum of **1** at −78 °C (—). Fluorescence spectrum of **1** at −196 °C (---).

Addition of *tert*-butyl hypochlorite to a stirred solution of 1-amino-2,2,5,5-tetramethylpyrrolidine and triethylamine in anhydrous dimethyl ether at −78 °C affords, in addition to an insoluble white precipitate (Et_3NHCl), a red solution (λ_{max} 497 nm, ϵ 20, Et_2O) of the 1,1-diazene **1** which is stable for days at −78 °C.[3c] This solution is filtered at −78 °C, further purified by low-temperature chromatography (−85 °C) on basic alumina (propane/dimethyl ether eluant), and concentrated in $CFCl_3$. Low-temperature ^1H NMR spectrscopy (−60 °C, $CFCl_3$) reveals 98% 1,1-diazene, 2% tetrazene, and small amounts of dimethyl ether. The absorption and fluorescence spectra of 1,1-diazene **1** in $CFCl_3$ are shown in Figure 2. The absorption spectrum of **1** (λ_{max} 497; 0–0 band, 565 nm; $CFCl_3$)[4] is sufficiently resolved to give the vibrational spacing of S_1, 1238 cm^{-1} (N–N stretch). For the fluorescence spectrum,[5] the 0–0 band at 607 nm is the maximum. The spacing between the peaks at 607 and 672 nm corresponds to 4.6 kcal, consistent with the 1638-cm^{-1} (4.7 kcal) N=N stretch of S_0 obtained from the infrared spectrum of **1**.[3c] The fact that the shape of the absorption and fluorescence spectra[6] are so different suggests that the thermally equilibrated S_0 and S_1 states of the 1,1-diazene **1** have *different geometries*. Goddard's calculations find that the thermally equilibrated S_0 and S_1 states of the 1,1-diazene are planar and pyramidal, respectively.[1f] The absorption and fluorescence spectra are separated by 42 nm, a Stokes shift probably due at least in part to differential solvation of S_0 and S_1.[4] A rough estimate of the fluorescence quantum yield (ϕ_F) is $\sim 10^{-3}$.[7] The value for k_f determined from the integrated

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(4) In CH_2Cl_2, 1,1-diazene **1** has a λ_{max} of 497 nm and 0–0 band of 572 nm. The λ_{max} and 0–0 band both blue shift in isopropanol to 487 and 552 nm, respectively.[3c]
(5) Fluorescence spectra were recorded with exciting wavelength 450 nm and Corning 3-71 emission filter and are corrected. Emission intensity goes to zero on warming.
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(7) Spectrum was corrected (Hamamatsu R955 PMT) and measured relative to rubrene Φ_f = 1, exciting wavelength 480 nm.

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