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Synthesis, Structure, and Reactivity of an Antiaromatic, 2,5-Dicarboxy-Stabilized 1,4-Dihydropyrazine

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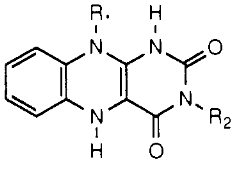
Abstract: 3-(Chloromethyl)-5,6-dihydro-5,5-dimethyl-1,4-oxazin-2-one (**4**) undergoes self-condensation in the presence of diisopropylethylamine to yield 4a,8a-diaza-2,6-dioxa-3,4,7,8-tetrahydro-4,4,8,8-tetramethylanthracene-1,5-dione (DDTTA). DDTTA is an example of a modestly stable, almost flat 1,4-dihydropyrazine. It is green in color, and the long-wavelength visible absorption band shows significant solvatochromism. DDTTA gives reversible one-electron-oxidation waves in methylene chloride at −0.33 and 0.61 V vs ferrocene/ferrocenium (0.07 and 1.01 V vs NHE, respectively) and reacts with Fe(1,10-phenanthroline)$_3^{3+}$ to yield DDTTA$^+$ (**5**) characterized by ESR spectroscopy. The radical cation is also produced in purple-black crystals by cocrystallization with tetracyanoquinodimethane (TCNQ). The black material has the composition DDTTA$^+$-(TCNQ)$_2^-$, and in solution it is unstable to molecular oxygen. Air-stable radical cation **5** is produced by air oxidation of DDTTA in trifluoroacetic acid. The resulting trifluoroacetate crystallizes as pale blue parallelepipeds with the composition DDTTA$^+$CF$_3$CO$_2^-$(CF$_3$CO$_2$H)$_2$; the radical cations are arranged in sheets with short C–H···O intermolecular contacts as established by X-ray analysis. DDTTA reacts with molecular oxygen in acetic acid to yield the unstable dioxetane **7**, 4a,8a-diaza-2,6-dioxa-9,9a-epidioxy-3,4,7,8,9,9a-hexahydro-4,4,8,8-tetramethylanthracene-1,5-dione, and in acetonitrile to yield the aldehyde **9**, 5,6-dihydro-2-oxo-5,5-dimethyl-1,4-oxazine-3-carboxaldehyde. Mechanisms for the air oxidations are proposed in Scheme I. [2 + 2]-Cycloaddition of DDTTA occurs with 1-phenyl-1,3,4-triazoline-2,5-dione (PTAD) to give the diazetidine **17**. Catalytic hydrogenation of DDTTA gives 4a,8a-diaza-2,6-dioxa-3,4,7,8,9,9a-hexahydro-4,4,8,8-tetramethylanthracene-1,5-dione (**13**), which air oxidizes to a mixture of DDTTA and 4a,8a-diaza-2,6-dioxa-3,4,7,8,9,9a-hexahydro-9a-hydroxy-4,4,8,8-tetramethylanthracene-1,5-dione (**14**) via the relatively persistent, purple radical cation **16**. DDTTA represents a new electron donor with three stable redox states and, consequently, has potential as a component in formation of organic electrically conducting materials.

Introduction

The 1,4-dihydropyrazine ring system has attracted much interest as a structural unit, largely as a result of the possibility of cyclic 8π-electron conjugation giving rise to so-called "antiaromatic"[1] character. These ring systems are thus electron rich and readily lose a single electron to give stable radical cations. The ring system is a key structural feature of certain redox-active biological molecules such as 1,5-dihydroflavins (**1**)[2] and some luciferins (**2**).[3]



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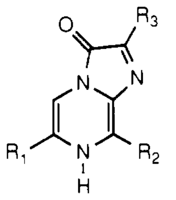

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Though 1,4-dihydropyrazine is itself unknown, stable 1,4-dihydropyrazines are known in which the pyrazine ring is stabilized by electron-withdrawing groups and/or conjugation. Of those systems for which molecular geometry is known, most adopt a boat-shaped conformation and thus avoid the destabilizing effects of 8π-electron conjugation.[4] Notable exceptions to this are the 1,4-bis(trialkylsilyl)-1,4-dihydropyrazines which have been shown to have a planar geometry[5] and exhibit properties associated with antiaromaticity such as paratropic NMR shifts.[6] We have shown[7] recently that the 2,5-diacyl-1,4-dihydropyrazine, 4a,8a-diaza-2,6-dioxa-3,4,7,8-tetrahydro-4,4,8,8-tetramethylanthracene-1,5-dione (DDTTA), also exhibits a planar geometry in its central ring. Unlike the silyl derivatives, DDTTA exhibits three stable redox states and is thus of potential interest with regard to the design of organic conducting charge-transfer complexes and/or salts.[8] We now report further on the synthesis and characterization of this molecule and some of the unusual chemistry, particularly redox chemistry, associated with its structure.

Results and Discussion

Synthesis and Characterization of DDTTA. 5,6-Dihydro-3,5,5-trimethyl-1,4-oxazin-2-one (**3**) was synthesized and chlorinated as described by Himmelsbach and co-workers.[9] Heating the resulting (chloromethyl)oxazinone **4** with diisopropylethylamine in DMF solvent under nitrogen resulted in an opaque, greenish black solution which, on workup, yielded a green crystalline solid identified by its IR, NMR, and mass spectra as DDTTA.

X-ray analysis of a single crystal of DDTTA reveals that the central ring is close to planar, giving a conjugated cyclic system with 8π electrons. Examination of the bond lengths indicates that the structure is probably best represented as a combination of the two resonance structures shown below (see Table I and Figure 1 of ref 7 for relevant bond lengths and angles and a thermal ellipsoid plot of DDTTA).

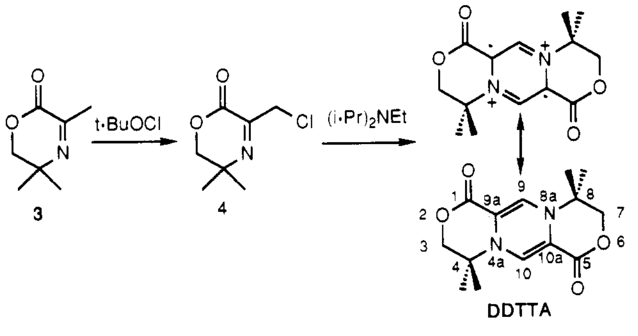

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Table I. Visible Spectral Data for DDTTA as a Function of Solvent and Related to Solvent Acceptor Number

solvent	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	acceptor no.[a]
tetrahydrofuran	550	73	8.0
benzene	562	101	8.2
acetone	566	111	12.5
dimethylformamide	570	108	16.0
acetonitrile	572	125	18.9
dimethyl sulfoxide	590	141	19.3
chloroform	596	130	23.1
formamide	612	154	39.8
acetic acid	616	179	52.9
trifluoroacetic acid	608	309	105.3

[a] Acceptor numbers were taken from ref 13.

Table II. Reduction Potentials for DDTTA and Related Compounds[a]

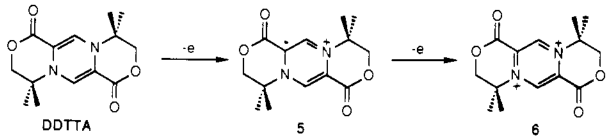
compd	$E°'$	compd	$E°'$
$DDTTA^+$ (**5**)	0.07	$DDTTA^{2+}$ (**6**)	1.01
$\mathbf{13}^+$	0.40	$\mathbf{14}^+$	0.52

[a] Reduction potentials were measured in methylene chloride relative to the reduction potential of internal ferrocenium and were converted to the normal hydrogen electrode (NHE) reference by adding 0.40 V.[33]

The N–C bonds (4a–9a and 8a–10a) are 0.1 Å longer than would be expected for a heteroaromatic system; thus the ring is elongated slightly. This geometry is similar to that observed in Sekiguchi's silylated benzene dianion[10] and is analogous to the geometry observed in cyclobutadiene,[11] though not in push–pull substituted cyclobutadienes.[12]

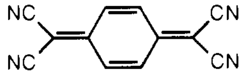
The most striking feature of DDTTA is its color; the solid is green, and solutions, which are air sensitive, vary in color from deep blue (acetic acid) to pale violet (THF). UV–visible spectroscopy reveals three absorption bands: two strong bands at 224 nm and 324 nm (extinction coefficients 7800 and 8330 M^{-1} cm^{-1}, respectively) which vary little with solvent and the third, a symmetry-forbidden π–π^* band. The configuration and symmetry of the latter transition were assigned on the basis of an extended Hückel calculation of the chromophore. This long-wavelength band varies in position from 550 to 620 nm, the wavelength increasing approximately with the Lewis acidity of the solvent as measured by acceptor numbers[13] (Table I). This suggests an intramolecular charge-transfer structure for the excited state which coordinates to Lewis acidic solvent molecules. All other 1,4-dihydropyrazines reported in the literature are colorless or, in the case of the 1,4-bis(trialkylsilyl) and 1,4-bis(trialkylgermyl) derivatives, yellow and red, respectively.[5] The visible transition for these latter 1,4-dihydropyrazines has been ascribed to intramolecular charge transfer from the ring to low-lying orbitals at the trialkylsilyl or trialkylgermyl substituents. Yamada and coworkers did report several compounds with electronic absorption spectra similar to that of DDTTA from the ultraviolet irradiation of 2,5-diacylpyrazines.[14] They proposed a dihydropyrazine–pyrazine charge-transfer structure for these compounds, but in the light of the above data these were probably 1,4-dihydropyrazines. They also isolated a solvent adduct for which they proposed a 1,4-dihydropyrazine structure; however, since this was colorless and air stable, the 1,2-dihydropyrazine structure seems more likely.

Oxidation Reactions of DDTTA. Like other 1,4-dihydropyrazines, the electron-rich ring system of DDTTA gives rise to extensive redox chemistry. Cyclic voltammetry in dichloromethane reveals two quasi-reversible, one-electron-oxidation waves (Table II) corresponding to oxidation to the radical cation **5** and dication **6**, respectively. Oxidation of DDTTA in acetonitrile with <1 equiv of aqueous ferriin, $Fe(1,10\text{-phenanthroline})_3^{3+}$, results in rapid formation of the radical cation **5**, characterized by a simple five-line ESR signal (coupling to two N atoms and with coupling to the ring hydrogens unresolved). The redox potentials correspond to an equilibrium constant for disproportionation of two radical cations **5** to DDTTA plus **6** of 1.5 × 10^{-16}, which clearly indicates that **5** is the most stable redox state.



DDTTA 5 6

Anaerobic reaction of DDTTA with tetracyanoquinodimethane (TCNQ) in acetonitrile results in single electron transfer to give a crystalline salt of composition $DDTTA^+(TCNQ)_2^-$. The proposal of an electron-transfer salt stems from X-ray and IR data. X-ray diffraction studies upon a single crystal of the salt reveal that the central ring has contracted, the N–C bond length (4a–9a and 8a–10a) decreasing from 1.443 to 1.393 Å (see Table I and Figure 2 of ref 7 for a comparison of bond lengths with those of DDTTA and a crystal packing diagram of $DDTTA^+(TCNQ)_2^-$). The IR carbonyl stretching frequency increases from 1676 cm^{-1} for DDTTA to 1720 cm^{-1} for $DDTTA^+(TCNQ)_2^-$, which is almost the carbonyl stretching frequency, 1725 cm^{-1}, observed for 2,5-bis(carbomethoxy)-3,6-dimethylpyrazine.[15] The C≡N stretching frequency decreases from 2223 cm^{-1} for TCNQ to 2202 cm^{-1} for $DDTTA^+(TCNQ)_2^-$. On the basis of the methodology of Cowan and co-workers,[16] the C≡N stretching frequency indicates that the degree of charge transfer in the salt is Z = 0.57/TCNQ, corresponding to a charge of Z = 1.14/DDTTA.



TCNQ

Air oxidation of DDTTA in trifluoroacetic acid cleanly produces a pale blue solution of the radical cation **5**. UV–visible spectroscopic monitoring of the oxidation revealed sharp isosbestic points at 326 and 386 nm. At completion, the radical cation showed a weak band at 720 nm responsible for the color along with two strong UV bands at 320 and 235 nm. Unlike $DDTTA^+(TCNQ)_2^-$, the trifluoroacetate salt in solution is air stable. The difference likely resides in differences in the oxygen stability of the respective anions. The radical cation structure was confirmed by observation of a five-line EPR spectrum characteristic of **5**. Slow evaporation of the solvent gave blue efflorescent prisms of composition $DDTTA^+CF_3CO_2^-(CF_3CO_2H)_2$. X-ray diffraction showed that the salt adopted a layered structure with alternating sheets of the radical cation and trifluoroacetate anions hydrogen bonded to two molecules of trifluoroacetic acid. Despite the change in counterion from TCNQ to solvated trifluoroacetate, the short intermolecular C–H···O distances between cations observed in the TCNQ salt[7] remain in the trifluoroacetate salt (Figure 1). In the trifluoroacetate salt, however, the interaction is attenuated with the cations being associated in discrete dimers rather than in infinite chains. Interactions between cations are thus significant despite the *gem*-dimethyl groups preventing the adoption of a full face-to-face stacking arrangement. The layered structure, alternating layers of cationic dimers and anions, is clearly related to the superconducting κ-phases of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) salts,[17] although in this case, the discrete nature of the anions and the lack of interaction between the cationic dimers prevent any significant conductivity. Two probe measurements at ambient temperature of a $DDTTA^+(TCNQ)_2^-$

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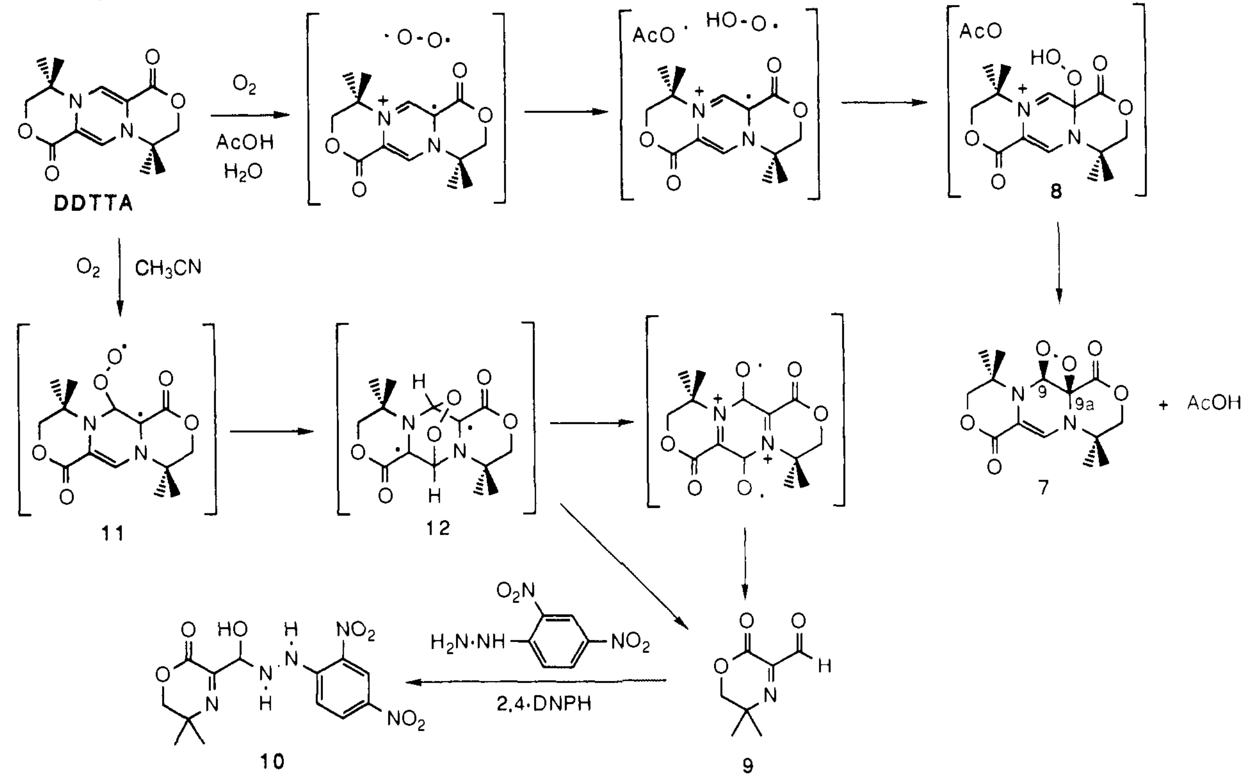
Scheme I. Proposed Mechanisms for the Air Oxidation of DDTTA



crystal which has an infinite chain of DDTTA$^+$ showed a conductivity of 10^{-3} Ω^{-1} cm^{-1}.[7]

In contrast, air oxidation of DDTTA in aqueous acetic acid using a very limited supply of oxygen to low conversion produces the dioxetane **7**, identified in the mixture with DDTTA by ^{1}H NMR and mass spectroscopy. The ^{1}H NMR spectrum shows four methyl singlets, two AB patterns, a dioxetane one-proton singlet, and an olefinic one-proton singlet, and the mass spectrum shows a molecular ion. When the reaction was allowed to proceed to completion, a complex mixture of products was formed. A reasonable mechanism for formation of **7** as shown in Scheme I involves initial single electron transfer to form **5** and superoxide as a triplet radical pair. DDTTA$^+$ was detected in the reaction mixture by ESR spectroscopy. In acetic acid/water (3:2, v/v), superoxide would subsequently be protonated; the pK_a of hydroperoxyl radical is 4.8.[18] Spin inversion would then be required prior to carbon–oxygen bond formation to give hydroperoxide **8**. Nucleophilic addition of the hydroperoxide functional group to the iminium cation followed by deprotonation by acetate would yield the dioxetane **7**. The reduction potential for $O_2/O_2^{\cdot-}$ in water is −0.16 V vs NHE at 1 M O_2;[19] consequently, the first step, one-electron oxidation of DDTTA by molecular oxygen, should be endergonic. The reaction must be thermodynamically driven by the formation of the two C–O bonds.

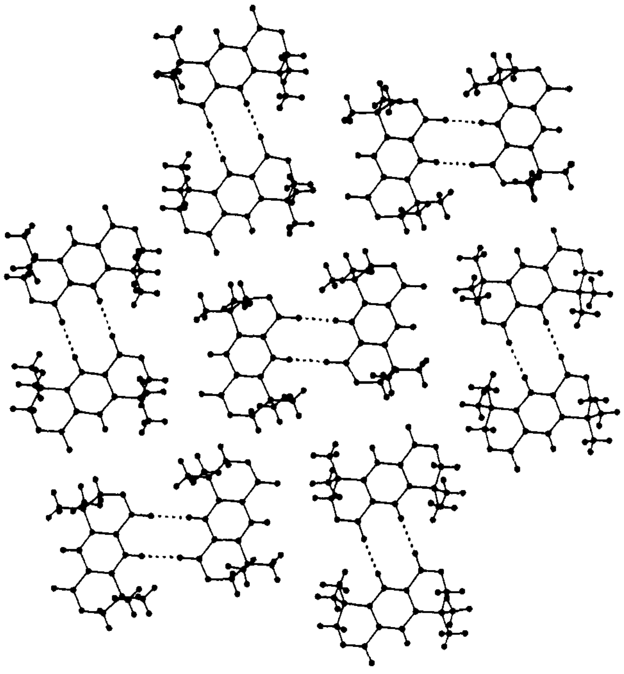


Figure 1. Packing of the DDTTA radical cations within the trifluoroacetate salt. The solvated anions are not shown for clarity. The short intermolecular C–H···O distances are shown as dotted lines.

The air oxidation was also performed in acetonitrile-d_3 with monitoring by ^{1}H NMR spectroscopy. The NMR spectrum showed relatively clean formation of 5,6-dihydro-2-oxo-5,5-dimethyl-1,4-oxazine-3-carboxaldehyde (**9**) as indicated by the appearance of three singlets at appropriate positions. Aldehyde **9** was characterized further by reaction with 2,4-dinitrophenylhydrazine (2,4-DNPH); upon addition of 2,4-DNPH, a hydrazine adduct, 5,6-dihydro-3-[[2-(2,4-dinitrophenyl)hydrazino]hydroxylmethyl]-2-oxo-5,5-dimethyl-1,4-oxazine (**10**), precipitated. The adduct structure was unambiguously established from spectra and elemental analysis as reported in the Experimental Section. ESR monitoring of the reaction did not reveal the presence of radical intermediates including DDTTA$^+$, which was observed in acetonitrile during ferriin oxidation of DDTTA (vide supra). Formation of **9** as opposed to dioxetane **7** is rationalized in Scheme I. Molecular oxygen is even more difficult to reduce by one electron in acetonitrile than in protic media; the reduction potential is −0.62 V vs NHE.[20] On the basis of the reduction potentials, the absence of a DDTTA$^+$ EPR signal, the product structure **9**, and the fact that DDTTA should be an excellent, captodatively substituted radicophile,[21] we propose initial radical addition of

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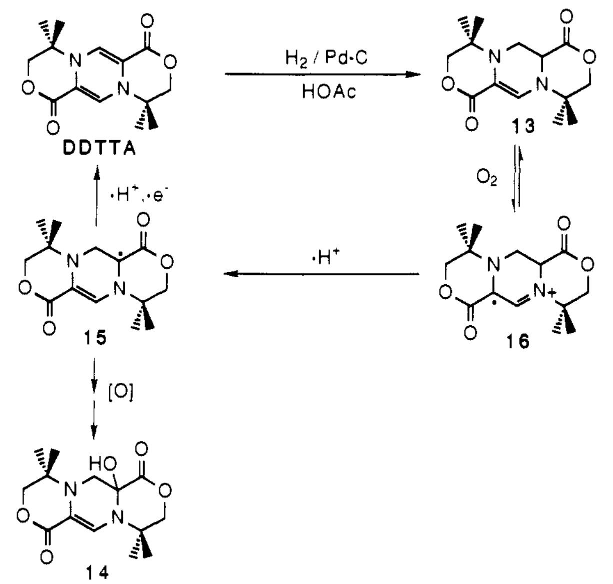
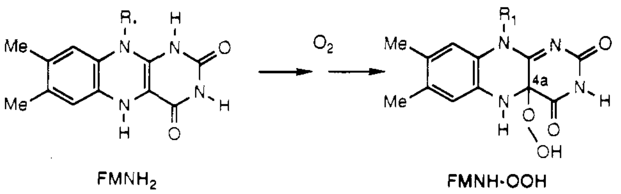
Scheme II. Formation and Air Oxidation of Dihydro-DDTTA (**13**)



molecular oxygen to DDTTA to form triplet biradical **11**. Radical **11** can then cyclize to the captodatively stabilized[21,22] or merostabilized[23] triplet diradical **12**. Concerted formation of **12** would also be a spin- and symmetry-allowed process. Spin inversion followed by double intramolecular electron transfer and double elimination is then proposed to yield aldehyde **9**. Spin inversion in radical **12** followed by radical-site induced fragmentation would also logically yield **9**.

The lack of covalent bond formation between DDTTA$^+$ and superoxide when formed in trifluoroacetic acid is surprising especially in light of formation of **7** in acetic acid. The difference may result from further protonation of hydroperoxy radical in the strongly acidic medium to form $H_2O_2^+$. Subsequently, $H_2O_2^+$ might logically oxidize a second molecule of DDTTA to DDTTA$^+$ with formation of hydrogen peroxide.

The electron-transfer mechanism proposed in Scheme I is related to molecular oxygen oxidations of other electron-rich species. Tetrakis(dimethylamino)ethylene is proposed to yield tetramethylurea via initial electron transfer and dioxetane formation.[24] In contrast with oxidation of the tetraaminoethylene, no chemiluminescence has been detected from oxidation of DDTTA. Dioxetanes from air oxidation of butylcyclobutadienes are proposed to exist in equilibrium with zwitterions analogous to the unprotonated form of **8** on the basis of NMR measurements as a function of temperature.[25] The reaction of molecular oxygen with luciferase-bound dihydroflavin mononucleotide (FMNH$_2$) to form the 4a-hydroperoxide FMNH-OOH is thought to occur by initial electron transfer from the 1,4-dihydropyrazine ring to molecular oxygen. The hydroperoxide is believed to be an intermediate in bacterial bioluminescence.[26]



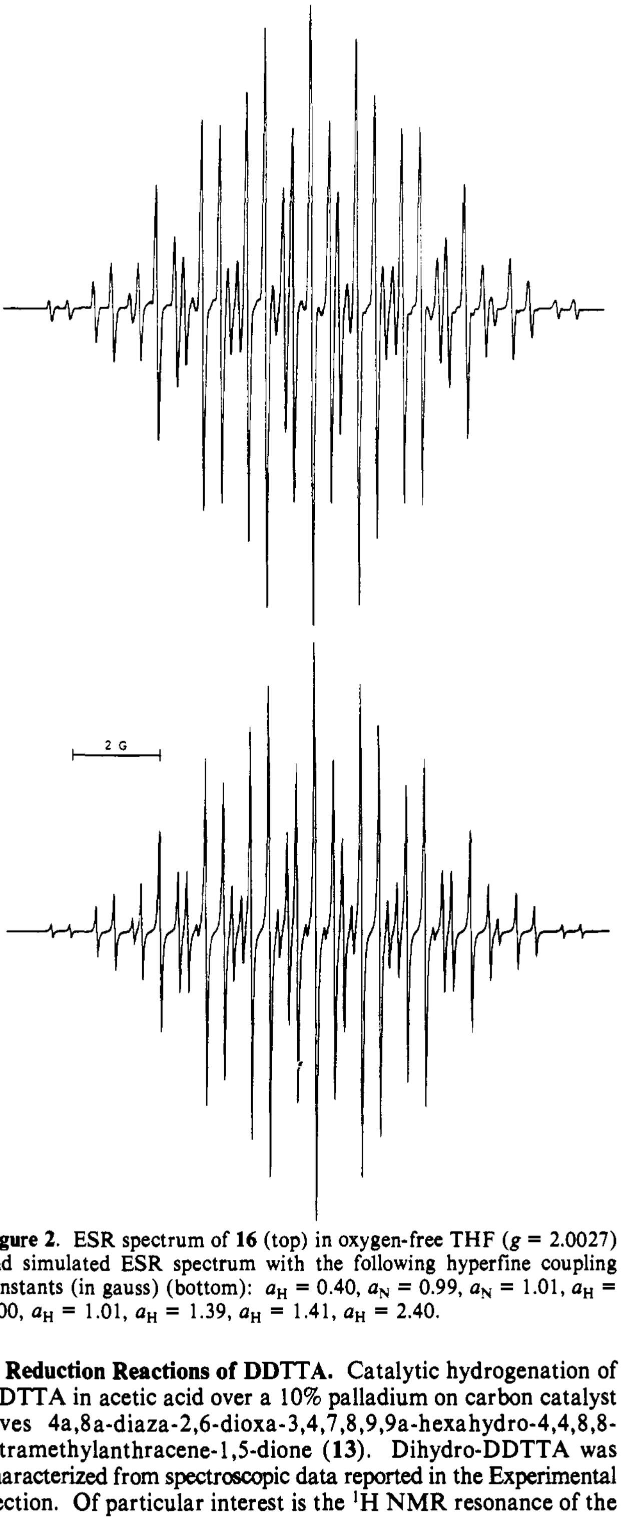


Figure 2. ESR spectrum of **16** (top) in oxygen-free THF (g = 2.0027) and simulated ESR spectrum with the following hyperfine coupling constants (in gauss) (bottom): a_H = 0.40, a_N = 0.99, a_N = 1.01, a_H = 1.00, a_H = 1.01, a_H = 1.39, a_H = 1.41, a_H = 2.40.

Reduction Reactions of DDTTA. Catalytic hydrogenation of DDTTA in acetic acid over a 10% palladium on carbon catalyst gives 4a,8a-diaza-2,6-dioxa-3,4,7,8,9,9a-hexahydro-4,4,8,8-tetramethylanthracene-1,5-dione (**13**). Dihydro-DDTTA was characterized from spectroscopic data reported in the Experimental Section. Of particular interest is the ^{1}H NMR resonance of the remaining vinylic proton at 7.14 ppm. The ^{1}H NMR spectrum of DDTTA shows the two vinylic ring protons at 6.28 ppm. The upfield shift of the proton is indicative of the paratropic character of DDTTA consistent with the idea of an 8π-electron ring system.

Somewhat surprisingly, **13** was found to undergo relatively rapid atmospheric oxidation to give ultimately DDTTA and the alcohol 4a,8a-diaza-2,6-dioxa-3,4,7,8,9,9a-hexahydro-9a-hydroxy-4,4,8,8-tetramethylanthracene-1,5-dione (**14**) in an approximately 1:2 ratio. The proportion of **14** in the reaction mixture was slightly lower when the oxidation occurred in aqueous acetic acid than when it occurred in chloroform, ruling out the possibility that the extra oxygen atom arises from water acting as a nucleophile. Intermediate in this oxidation are the radical **15**, detected by ESR in a solution of **13** in THF, and the purple radical cation **16**, which was also detected in a sample of **13** that had been partially air

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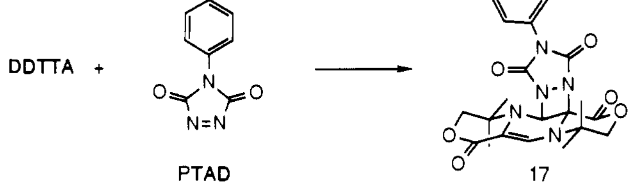
oxidized in acetic acid. The ESR spectrum for **16** is modestly complex, with several fortuitous degeneracies in the hyperfine coupling constants; the observed and simulated spectra are shown in Figure 2. These observations suggest a mechanism for oxidation of **13** as proposed in Scheme II whereby reaction with oxygen gives **16** and superoxide. The radical cation subsequently loses a proton to give the captodatively stabilized[20,21] radical **15**, which either is further oxidized to give DDTTA or combines with molecular oxygen or an oxy radical to give ultimately **14**.

Cyclic voltammetry performed on methylene chloride solutions of **13** and **14** reveals reversible and quasi-reversible one-electron-oxidation waves, respectively (Table II). This facile, reversible, one-electron oxidation of the α,β-diamino-substituted unsaturated ester functionality to give a relatively stable radical cation is probably due to a combination of the captodative stabilization of the radical center at the α-position along with stabilization of the positive charge by the remaining nitrogen. This being known, the stability of the previously noted dioxetane at room temperature is surprising. One would expect, especially with a strained four-membered-ring system, that a rapid intramolecular electron transfer would occur, oxidizing the alkene and reducing the dioxetane ring. However, bearing in mind that the extra oxygen atom in **14** increases the redox potential of the alkene by 0.12 V (presumably due to inductive effects), one might suggest that the dioxetane/diamine functionality of **7** is sufficiently electron balanced to inhibit internal redox chemistry.

[2 + 2]-Cycloaddition. On addition of DDTTA to a solution of 1-phenyl-1,3,4-triazoline-2,5-dione (PTAD) in dichloromethane, a rapid reaction occurs to produce the diazetidine, 4a,8a-diaza-2,6-dioxa-3,4,7,8,9,9a-hexahydro-9,9a-(1′-phenyl-2′,5′-dioxo-1′,3′,4′-triazoline-3′,4′-diyl)-4,4,8,8-tetramethylanthracene-1,5-dione (**17**). The formation of **17** is formally a symmetry-forbidden [2 + 2]-cycloaddition;[27] however, just as [2 + 2]-cycloadditions to cyclobutadiene are commonly viewed as [2 + 4]-cycloadditions,[28] formation of **17** can be viewed as an allowed [2 + 8]-cycloaddition. As in cycloadditions of cyclobutadiene to highly electron poor dienophiles,[29] formation of **17** may also occur via initial electron transfer from DDTTA to PTAD with the intermediacy of a radical ion pair.



PTAD

17

Diazetidine **17** was irreversibly oxidized at a peak potential of 0.98 V vs ferrocene/ferrocenium (1.38 V vs NHE). The difficulty of oxidation reflects the electron-withdrawing effect of the triazolinedione ring and reinforces the earlier hypothesis that an electron-donating effect from the diamino-ene functionality occurs through the saturated carbon atoms at the 9- and 9a-positions to stabilize the dioxetane **7**.

In summary, DDTTA represents a dicarboxy-stabilized 1,4-dihydropyrazine which shows some antiaromatic character. Stabilization is likely related to the general stabilization of $4n(\pi)$-electron systems through the effect of donor and acceptor groups acting in concert.[30] In DDTTA the donor groups are within the $4n(\pi)$-electron system. Like dihydroflavins, DDTTA can be reversibly oxidized in two one-electron steps, although it is a significantly weaker reducing agent, probably because it has two electron-withdrawing substituents. DDTTA readily reacts with electron-poor species such as ferriin, molecular oxygen, TCNQ, and PTAD. The radical cation is the most stable of the redox states showing stability to molecular oxygen. The dihydro derivative **13** is also readily oxidized in one-electron steps with the intermediacy of a modestly stable, purple radical cation. Because of their redox properties and symmetry, DDTTA, in particular, and the 2,5-dicarboxy-1,4-dihydropyrazine structure, in general, have potential application in the design of electrically conducting organic materials.[8]

Experimental Section

General Remarks. UV–visible spectra (200–800 nm) were recorded on a Hewlett-Packard 8452A diode array spectrophotometer using 10-mm square cuvettes and nitrogen-purged, spectrograde solvents; extinction coefficients are reported in $M^{-1}\ cm^{-1}$. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR-300S spectrometer; chemical shifts are reported in ppm on the δ scale using tetramethylsilane as an internal reference, and coupling constants are reported in hertz. Solutions of DDTTA and dihydro-DDTTA (**13**) for NMR analysis were prepared under a nitrogen atmosphere. IR spectra were recorded on a Perkin-Elmer Model 1600 FTIR spectrophotometer. Mass spectra were obtained with a VG-7070 EQ-HF hybrid tandem mass spectrometer. ESR spectra were recorded on a Varian E-109E spectrometer. Cyclic voltammetry was performed using a Cypress CYSY-1 computer-controlled electroanalysis system with an Ag/Ag^+ reference electrode, a platinum wire auxiliary electrode, and a platinum disk working electrode. Nitrogen-purged methylene chloride was used as solvent, and tetrabutylammonium perchlorate was used as the supporting electrolyte. The ferrocene/ferrocenium couple was used as an internal standard. Elemental analyses were performed by Atlantic Microlab, Norcross, GA. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl and stored under nitrogen. Methylene chloride and diisopropylethylamine were distilled from calcium hydride prior to use. Dimethylformamide (DMF) and acetonitrile were stored over 3A molecular sieves before use. 3-(Chloromethyl)-5,6-dihydro-5,5-dimethyl-1,4-oxazin-2-one (**4**) was synthesized using the procedure of Himmelsbach and co-workers[9] and used immediately after preparation.

4a,8a-Diaza-2,6-dioxa-3,4,7,8-tetrahydro-4,4,8,8-tetramethylanthracene-1,5-dione (DDTTA). To a 250-mL round-bottomed flask equipped with a reflux condenser and a nitrogen inlet was added 10.0 g (57 mmol) of 3-(chloromethyl)-5,5-dimethyl-5,6-dihydro-1,4-oxazin-2-one (**4**) dissolved in 250 mL of DMF. The solution was purged with nitrogen for 10 min, and 7.4 g (57 mmol) of diisopropylethylamine was added. The solution was heated under a nitrogen atmosphere at 95 °C for 24 h. The resulting black-green solution was rotary evaporated under high vacuum (0.1 Torr) at room temperature until small green crystals began to precipitate. Diethyl ether (300 mL) was added, and the resulting suspension was suction filtered. The solid collected on the filter paper was washed with 100 mL of water and then stirred with 50 mL of toluene. The solid was again collected by suction filtration and air dried, to leave DDTTA as a bottle green, crystalline solid (1.8 g, 22%). The material was stored in a standard laboratory freezer because it deteriorated in air at ambient temperature. The following physical data were obtained: mp 280 °C dec; ^1H NMR (CD_2Cl_2) δ 1.22 (s, 12 H), 3.79 (s, 4 H), 6.28 (s, 2 H); ^{13}C NMR (CD_2Cl_2) δ 21.6 (4 C), 51.4 (2 C), 74.1 (2 C), 107.9 (2 C), 136.9 (2 C), 159.8 (2 C); IR (KBr pellet) 1676 cm^{-1} (C=O), 1587 cm^{-1} (C=C); UV-vis (THF) λ_{max} 224 (ϵ = 7800), 324 (ϵ = 8330), 550 nm (ϵ = 73); UV–vis, other solvents, see Table I; mass spectrum (70 eV), *m/z* (relative intensity) 278 ($M^{\bullet+}$, 93), 223 (30), 178 (79), 151 (100), 123 (68), 106 (62), 78 (36), 55 (46). No satisfactory elemental analysis could be obtained due to surface air oxidation DDTTA.

X-ray Crystallography. Crystals were grown as deep-green plates by layering *n*-heptane onto a dichloromethane solution of DDTTA under a nitrogen atmosphere and allowing the two layers to diffuse together. Details of the data collection and solution and refinement procedures are given elsewhere.[7]

Oxidation of DDTTA with Ferriin, Fe^{3+}(1,10-phenanthroline)$_3$. 1,10-Phenanthroline hydrate (1.49 g, Fisher) was added to a solution of 1.01 g of $Fe(NO_3)_3 \cdot 9H_2O$ in 100 mL of distilled deionized water. The resulting solution of ferriin (2.5×10^{-2} M) was stored refrigerated in the dark.

The ferriin solution (2.0 mL, 50 μmol) was diluted to 100 mL with distilled water and purged with nitrogen. This solution gave an absorbance of 0.101 at 508 nm. To the solution was added 2.5 mg (9 μmol) of DDTTA. The solution was stirred until dissolution was complete, at

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which point the absorbance at 508 nm was 1.28, corresponding to a one-electron oxidation of DDTTA to **5**.

In an ESR sample tube fitted with a silicone rubber septum, 0.5 mg (1.8 μmol) of DDTTA was dissolved in 1.0 mL of nitrogen-purged acetonitrile. A 5-μL (0.13 μmol) aliquot of the original ferriin solution was then injected through the septum. After shaking, the orange color of ferroin, Fe^{2+}(1,10-phenanthroline)$_3$, was apparent in the solution. ESR spectroscopy showed a five-line signal, relative intensity 1:2:3:2:1, corresponding to the radical cation **5**. The following parameters were recorded: a_N = 7.12 G, g = 2.0035; coupling to hydrogen was not resolved, and a_H must be less than or equal to the observed line width; simulation with a_H = 0.25 G and a natural line width of 0.25 G reproduces the observed line width.

Reaction of DDTTA with 7,7,8,8-Tetracyanoquinodimethane (TCNQ). Tetracyanoquinodimethane (102 mg, 0.50 mmol) was dissolved in 15 mL of acetonitrile in a 25-mL round-bottomed flask by heating of the solution with a hot water bath (60 °C). Under a nitrogen atmosphere, 139 mg (0.50 mmol) of DDTTA was added in one portion, and the resulting deep green solution was induced to form crystals by insulation of the flask with glass wool and cooling of the water bath to room temperature. Filtration of the resulting suspension gave the TCNQ salt (112 mg) as black needles with a metallic purple luster. This had IR bands (KBr pellet) at 2202 cm^{-1} (CN triple bond stretch) and 1720 cm^{-1} (C=O stretch). Elemental analysis revealed a 1:2 stoichiometry of DDTTA to TCNQ. Calcd for $C_{38}H_{26}N_6O_4$: C, 66.47; H, 3.82; N, 20.40. Found: C, 66.54; H, 3.83; N, 20.32. Details of the collection of single-crystal X-ray diffraction data and its solution and refinement are given elsewhere.[7]

Air Oxidation of DDTTA in Trifluoroacetic Acid. DDTTA (81 mg) was dissolved in trifluoroacetic acid (10 mL) to give a deep blue solution. This was allowed to evaporate in air overnight, to leave blue prisms of the radical cation trifluoroacetate. A single crystal was removed for X-ray structure analysis. The remainder was washed with ether and dried under vacuum to remove adhering trifluoroacetic acid solvent. This left 155 mg of the salt as a pale greenish blue solid. Anal. Found: C, 39.44; H, 3.33; N, 4.91; corresponding approximately to a composition DDTTA$^+$CF$_3$CO$_2^-$(CF$_3$CO$_2$H)$_{1.8}$. Calcd: C, 39.44; H, 3.32; N, 4.70. UV-vis (CH$_3$CN) showed λ_{max} 224 (ϵ = 10400), 240 (ϵ = 8720), 324 (ϵ = 14300), 388 (ϵ = 2340), 408 (ϵ = 1800), 722 nm (ϵ = 40). X-ray analysis at −125 °C gave the following unit cell parameters: $C_{14}H_{18}N_2O_4 \cdot CF_3CO_2 \cdot 2CF_3CO_2H$, M_w = 619.4; monoclinic, $P2_1/c$; a = 8.042 (9) Å, b = 21.93 (2) Å, c = 14.54 (2) Å; β = 90.27 (9)°; V = 2564 (5) Å^3; ρ_{calcd} = 1.605 g cm^{-3}; 2542 reflections were observed with $F > 4.0\sigma(F)$. Solution (by direct methods) and refinement gave R = 10.53%, wR = 15.68%. The large residuals appear to be the result of considerable rotational disorder involving two of the three trifluoromethyl groups. These two groups account for approximately 17% of the total electron density in the unit cell, and so the high R value is not unreasonable. Attempts to model this disorder resulted in many frustrating failures and no adequate model. The problem was not significantly improved by collecting the data at low temperatures. Because of the poor model of the solvent, we have made only a few general statements about the DDTTA$^+$ cation; however, we are quite confident in its basic geometry. Solvent disorder problems in X-ray crystallography have been discussed recently;[31] structures that are solvates typically have higher R values. In fact, van der Sluis and Spek have recently reported that least-squares refinement of the atomic parameters of the ordered part of a crystal, which contains disordered solvent, improves the R value from 8–11% to 4–6%.[32] As of this date, attempts to obtain the van der Sluis refinement program have been unsuccessful. Full details of data collection and refinement are provided as supplementary material.

Controlled Air Oxidation of DDTTA in Aqueous Acetic Acid. Under an atmosphere of USP grade nitrogen (>95% pure), 98 mg of DDTTA was dissolved in 15 mL of a nitrogen-purged mixture of acetic acid/water (3:2 v/v). The deep blue solution was stirred at ambient temperature for 48 h, and then the solvent was rotary evaporated. A ^{1}H NMR spectrum of the resulting green solid (120 mg) in CDCl$_3$ showed three very broad resonances from DDTTA and its radical cation, along with sharp resonances corresponding to 4a,8a-diaza-2,6-dioxa-9,9a-epidioxy-3,4,7,8,9,9a-hexahydro-4,4,8,8-tetramethylanthracene-1,5-dione (**7**): ^{1}H NMR δ 7.15 (s, 1 H), 5.18 (s, 1 H), 4.68 (d, J = 11.5 Hz, 1 H), 4.15 (d, J = 11.0 Hz, 1 H), 4.09 (d, J = 11.5 Hz, 1 H), 4.00 (d, J = 11.0 Hz, 1 H), 1.42 (s, 3 H), 1.41 (s, 3 H), 1.39 (s, 3 H), 1.31 (s, 3 H); negative-ion CI mass spectrum showed a molecular ion at m/z 310. The presence of the radical cation was confirmed by detection of its characteristic five-line ESR signal.

Air Oxidation of DDTTA in Acetonitrile. DDTTA (10.8 mg) was dissolved in acetonitrile-d_3 (1.0 mL) and stirred in air until the solution turned from blue to pale yellow (24 h). The ^{1}H NMR spectrum of the resulting solution showed three sharp resonances corresponding to the predominant product, 5,6-dihydro-2-oxo-5,5-dimethyl-1,4-oxazine-3-carboxaldehyde (**9**): ^{1}H NMR (CD$_3$CN) δ 1.33 (s, 6 H), 4.26 (s, 2 H), 9.61 (s, 1 H); IR (thin film on a NaCl plate) 1758 (aldehyde C=O), 1740 cm^{-1} (ester C=O). Monitoring of the reaction by ESR spectroscopy did not show the presence of any radical intermediates. The reaction was also performed in the dark, and no difference was observed. The experiment was repeated on a larger scale, 128 mg of DDTTA being stirred in 5 mL of acetonitrile until the oxidation was complete (48 h). To this solution was added 182 mg of 2,4-dinitrophenylhydrazine (2,4-DNPH), and the solution was stirred at ambient temperature for 1 h, during which time the yellow hydrazine adduct, 5,6-dihydro-3-[2-[(2,4-dinitrophenyl)hydrazino]hydroxymethyl]-2-oxo-5,5-dimethyl-1,4-oxazine (**10**), precipitated. Filtration gave 148 mg of material (45%) with mp 237 °C (discolors ~170 °C) and the following properties: ^{1}H NMR (DMSO-d_6) δ 9.79 (s, exchanges with D$_2$O, 1 H), 8.82 (d, J = 3 Hz, 1 H), 8.30 (dd, J = 10 Hz, J = 3 Hz, 1 H), 7.71 (d, J = 10 Hz, 1 H), 6.52 (d, J = 7 Hz, exchanges with D$_2$O, 1 H), 6.09 (d, J = 7 Hz, exchanges with D$_2$O, 1 H), 5.32 (t, J = 7 Hz, collapses to singlet with D$_2$O, 1 H), 4.26 (d, J = 11.5 Hz, 1 H), 4.16 (d, J = 11.5 Hz, 1 H), 1.22 (s, 3 H), 1.14 (s, 3 H); ^{13}C NMR (DMSO-d_6) δ 156.2, 154.6, 150.0, 135.6, 129.9, 128.7, 123.3, 116.5, 78.8, 73.4, 54.5, 24.1, 23.9; IR (KBr) 3462 (OH), 3370 (NH), 3287 (NH), 1733 (ester C=O), 1654 cm^{-1} (C=N); mass spectrum, positive-ion CI (methane) m/z (relative abundance) 336 (M + 1 − H$_2$O, 20), 199 (50), 156 (M + 1 − 2,4-DNPH, 100). Calcd for $C_{13}H_{15}N_5O_7$: C, 44.18; H, 4.28; N, 19.83. Found: C, 44.27; H, 4.29; N, 19.88.

4a,8a-Diaza-2,6-dioxa-3,4,7,8,9,9a-hexahydro-4,4,8,8-tetramethylanthracene-1,5-dione (13). Palladium on carbon (10%, 35 mg) was suspended in 5 mL of glacial acetic acid and saturated with hydrogen. A 99-mg sample of DDTTA was dissolved in 20 mL of nitrogen-purged acetic acid, and the solution was added rapidly to the catalyst suspension. The mixture was stirred vigorously under 1 atm of hydrogen until hydrogen uptake ceased (6 h). The solvent was removed promptly under vacuum, and the residue was transferred to a glovebox. Under a nitrogen atmosphere 30 mL of oxygen-free THF was shaken with the residue, and the suspension was filtered through a coarse sintered glass frit. Evaporation of the filtrate gave **13** (48 mg, 44%) as a pale violet solid (slightly contaminated with the radical cation **16**): ^{1}H NMR (CDCl$_3$) δ 1.16 (s, 3 H), 1.18 (s, 3 H), 1.32 (s, 3 H), 1.38 (s, 3 H), 2.69 (dd, J = 3.7 Hz, J = 8.3 Hz, 1 H), 3.72 (dd, J = 3.7 Hz, 11 Hz, 1 H), 4.40 (dd, J = 8.3 Hz, J = 11 Hz, 1 H), 3.94 (d, J = 11 Hz, 1 H), 4.11 (d, J = 11 Hz, 1 H), 4.10 (d, J = 12 Hz, 1 H), 4.28 (d, J = 12 Hz, 1 H), 7.14 (s, 1 H); ^{13}C NMR (CDCl$_3$) δ 167.7, 163.1, 124.9, 109.5, 75.8, 74.1, 54.1, 53.7, 51.4, 42.8, 24.0, 23.6, 22.0, 16.9; IR (KBr pellet) 1758 (ester C=O), 1696 (conjugated ester C=O), 1599 cm^{-1} (C=C); UV (CH$_3$CN) λ_{max} 334 (ϵ = 9550), 228 nm (ϵ = 5700); mass spectrum (70 eV) m/z (relative abundance) 280 (M$^{\bullet+}$, 100), 278 (54), 265 (85), 223 (17), 178 (41), 151 (63), 123 (37), 106 (30), 78 (26), 55 (30). Measurement of the exact mass of the molecular ion gave m/z = 280.1437 (calcd for $C_{14}H_{20}N_2O_4$, m/z = 280.1423); **13** could not be obtained pure enough for elemental analysis. A small sample of crude **13** was dissolved in oxygen-free THF in an ESR sample tube. The resulting ESR spectrum showed a small concentration of radical cation **16** superimposed on a signal corresponding to radical **15**, coupling constants a_H = 1.9 G (1:1), a_N = 4 G (1:1:1), a_N = 5 G (1:1:1), a_{CH_2} = 5 G (1:2:1).

Air Oxidation of 13 in CDCl$_3$. A small sample (~5 mg) of **13** was dissolved in 1 mL of deuteriochloroform in an NMR sample tube and shaken periodically over a period of 12 h. The ^{1}H NMR spectrum of the resulting solution showed the presence of DDTTA and **14** as the sole oxidation products. Integration gave the ratio DDTTA:**14** as approximately 2:5.

Air Oxidation of 13 in Aqueous Acetic Acid. A 15-mg sample of **13** was dissolved in 3 mL of acetic acid, and 2 mL of distilled water was added. This solution was stirred in air for 15 min. The resulting blue solution was evaporated, and the residue was redissolved in deuteriochloroform. Integration of the ^{1}H NMR spectrum gave the ratio of DDTTA:**14** as approximately 2:3.

4a,8a-Diaza-2,6-dioxa-3,4,7,8,9,9a-hexahydro-9a-hydroxy-4,4,8,8-tetramethylanthracene-1,5-dione (14). Palladium on carbon catalyst (50 mg, 10%) was suspended in 5 mL of acetic acid and saturated with hydrogen. A 204-mg sample of DDTTA was dissolved in 20 mL of nitrogen-purged acetic acid, and the solution was added rapidly to the catalyst suspension. The mixture was stirred vigorously under a hydrogen atmosphere (650 mmHg) at 25 °C until 21 cm^3 (1 equiv) of hydrogen had been taken up by the mixture. The catalyst was removed by filtration through a Celite pad to yield a pale yellow solution, which rapidly (~30 s) turned blue on exposure to air. Prompt evaporation gave 162 mg of a violet solid consisting of a mixture of DDTTA, **13**, and **14** (by ^{1}H NMR); integration revealed a ratio of DDTTA:**14** of approximately 2:5. Also present was the radical cation **16** detected by ESR. These were separated by flash chromatography on silica gel (230–400 mesh), eluting with a nitrogen-degassed mixture of 7:3 CH_2Cl_2/EtOAc and with a constant stream of nitrogen passing over the collected eluent. The chromatography gave the alcohol, **14** (48 mg), as a pale yellow solid: ^{1}H NMR ($CDCl_3$) δ 7.14 (s, 1 H), 4.86 (d, J = 11.5 Hz, 1 H), 4.18 (d, J = 11.2 Hz, 1 H), 4.05 (d, J = 11.5 Hz, 1 H), 4.02 (d, J = 11.2 Hz, 1 H), 3.41 (d, J = 10.7 Hz, 1 H), 3.24 (s, exchanges with D_2O, 1 H), 2.33 (d, J = 10.7 Hz, 1 H), 1.33 (s, 3 H), 1.32 (s, 3 H), 1.19 (s, 3 H), 1.18 (s, 3 H); ^{13}C NMR (attached protons established with DEPT pulse sequence) δ 165.3 (C=O), 162.4 (C=O), 124.6 (vinylic CH), 111.3 (vinylic C), 79.0 (C), 75.5 (CH_2), 72.8 (CH_2), 54.2 (C), 51.6 (C), 48.9 (CH_2), 25.8 (CH_3), 24.4 (CH_3), 22.5 (CH_3), 17.8 (CH_3); IR (KBr pellet) 3379 (OH), 1756 (ester C=O), 1689 (conjugated ester C=O), 1603 cm^{-1} (C=C); UV (MeOH) λ_{max} 334 (ϵ = 12 500), 214 nm (ϵ = 8270); mass spectrum (70 eV) m/z (relative abundance) 296 ($M^{\bullet +}$, 100), 281 (70), 278 (24), 181 (30), 151 (26), 123 (30), 95 (23), 78 (18), 55 (60). Calcd for $C_{14}H_{20}N_2O_5$: C, 56.75; H, 6.80. Found: C, 56.47; H, 6.81.

Further elution gave a crystalline, violet solid (113 mg) containing the tetrahydropyrazine derivative **13** and the corresponding radical cation **16**, responsible for the violet color, λ_{max} 562 (CH_3CN) and 612 nm (HOAc), and having an ESR spectrum in oxygen-free THF as shown in Figure 2.

4a,8a-Diaza-2,6-dioxa-3,4,7,8,9,9a-hexahydro-9,9a-(1'-phenyl-2',5'-dioxo-1',3',4'-triazoline-3',4'-diyl)-4,4,8,8-tetramethylanthracene-1,5-dione (17). Under a nitrogen atmosphere, 139 mg of DDTTA was added to a solution of 88 mg of 1-phenyl-1,3,4-triazoline-2,5-dione (PTAD) in 20 mL of dichloromethane. The deep color of the solution faded after approximately 1 min to a pale yellow. Evaporation of the solvent gave an orange glass that was purified by filtration through a silica gel column using 9:1 dichloromethane/ethyl acetate (v/v) as solvent. Evaporation and recrystallization from dichloromethane/heptane gave pale yellow needles (120 mg, 53%): mp 170 °C dec; ^{1}H NMR ($CDCl_3$) δ 1.18 (s, 6 H), 1.34 (s, 3 H), 1.57 (s, 3 H), 4.05 (d, J = 10.8 Hz, 1 H), 4.06 (d, J = 11.6 Hz, 1 H), 4.19 (d, J = 11.6 Hz, 1 H), 4.36 (J = 10.8 Hz, 1 H), 6.35 (s, 1 H), $\sim$7.5 (m, 5 H), 7.65 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 160.0, 153.3, 152.9, 151.3, 146.2, 129.4 (2 C), 128.6, 125.2 (2 C), 113.2, 110.6, 77.8, 74.1, 65.5, 55.9, 55.2, 25.5, 23.3, 21.7, 21.4; IR (KBr) 1781 (C=O), 1734 (C=O), 1627 cm^{-1} (C=C); mass spectrum (70 eV) m/z (relative intensity) 453 ($M^{\bullet +}$, 15), 327 (6), 278 (100), 223 (16), 178 (32), 151 (25), 119 (39). Measurement of the exact mass of the molecular ion gave m/z = 453.1632 (calcd for $C_{22}H_{22}N_5O_6$, m/z = 453.1648); **17** could not be obtained pure enough for elemental analysis.

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Supplementary Material Available: A complete description of the X-ray crystallographic determination of the trifluoroacetate salt of DDTTA including atomic coordinates, isotropic and anisotropic displacement parameters, bond lengths, and bond angles (11 pages); listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

Norrish II Reactions of Liquid-Crystalline Ketones. Comparison between Smectic B and Solid Phase Order and Control of Photoproduct Distributions[1]

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Abstract: The Norrish II photoreactions of *trans*-1-(4-heptanoylphenyl)-4-heptylcyclohexane (**2a**) and *trans*-1-heptyl-4-(4-nonanoylphenyl)cyclohexane (**2b**) have been examined in their isotropic, smectic B, and solid phases. The smectic phases have been characterized by optical microscopy, differential scanning calorimetry, and X-ray diffraction. Solid and smectic phase order, probed by deuterium NMR spectroscopy of **2** deuteriated at the methylene α to the carbonyl group, is correlated with the photochemical results. The apparent absence of a directing influence of the smectic B phases on the course of the Norrish II reactions of **2** is attributed to the local fluidity afforded the methylene groups of the alkyl chains. The solid phase influence on the distribution of Norrish II photoproducts is significant and indicates that a small amount of motional freedom persists in the alkyl chains even after bulk crystallization.

Introduction

Liquid-crystalline phases can provide constrained environments capable of directing the motions, conformations, and reactions of appropriately designed solute molecules.[2] For example, the structural link between ketones in nematic, smectic, and solid phases of mesogenic hosts and their Norrish type II photoreactions have been extensively investigated.[2] Recently, we reported the results from a study of the Norrish II reactivity of two neat liquid-crystalline ketones (**1a** and **1b**, Scheme I) in their isotropic, nematic, and solid phases.[3] In such systems, the disturbances that a foreign solute may impose on the packing order of its anisotropic host molecules are absent; in principle, any selectivity detected in reactions of molecules in a neat phase may be attributed to restrictions imposed by the undisturbed host lattice.

Herein, we report the Norrish II photoreactivity (Scheme I) of *trans*-1-(4-heptanoylphenyl)-4-heptylcyclohexane (**2a**) and *trans*-1-heptyl-4-(4-nonanoylphenyl)cyclohexane (**2b**) in their isotropic, smectic B, and solid phases. The elimination to cyclization (E/C) product ratios are used to measure the influence of phase order on the course of the reaction. In this study, selectivity is defined as the ratio of E/C values in the anisotropic

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(1) Part 45 in our series, Liquid-Crystalline Solvents as Mechanistic Probes. Dedicated to Prof. K. Venkatesan on the occasion of his 60th birthday. For Part 44, see: Weiss, R. G.; Chandrasekhar, S.; Vilalta, P. M. *Collect. Czech. Chem. Commun.*, submitted for publication.

(2) For reviews, see: (a) Weiss, R. G. *Tetrahedron* **1988**, *44*, 3413. (b) Weiss, R. G. In *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH: Weinheim, 1991; Chapter 14 and references therein.

(3) Furman, I.; Weiss, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1381.

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