produced in yields of 100% and 5%, respectively.

Esterification of Carboxylic Acids. A mixture of carboxylic acid (1 mmol), alcohol (20–30 mmol), 1 (0.1 mmol), and an alkane (a GLC internal standard) was heated, with stirring, at 80 °C for 24 h. The yield of the ester was determined by GLC analysis. Similar results were obtained when an inert solvent (2 mL) was used. However, the use of a larger amount of inert solvent led to a decrease in the rate of reaction.

Attempted Hydrolysis of Butyl Butyrate. A mixture of butyl butyrate (360 mg, 2.50 mmol), water (0.5 mL), 1 (0.025 mmol), decane (GLC internal standard, 1.00 mmol), and solvent (benzene, THF, 1,4-dioxane, and diglyme; 5 mL) was refluxed for 20 h. GLC analysis showed that the butyl butyrate remained intact (99–100% yield).

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Spectroscopy and Photochemistry of 2-Quinolones and Their Lewis Acid Complexes[1]

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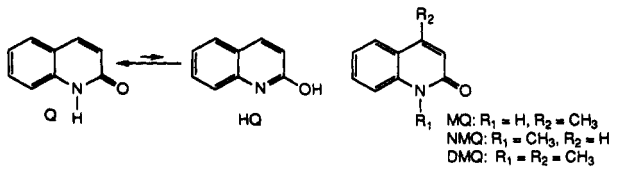
The spectroscopic properties, photodimerization, and cross-cycloaddition reactions of 2-quinolone and three of its methylated derivatives have been investigated in the absence and presence of the strong Lewis acid BF_3. Comparison of quinolone, which forms a hydrogen-bonded dimer, and its N-methylated derivatives establishes that hydrogen bonding has little effect on these properties. Methylation at C-4 also has little effect on spectroscopic properties, but does retard photodimerization and result in the formation of photoene products in competition with cycloadduct formation with alkenes. All of the quinolones form strong complexes with BF_3. Complex formation results in changes in the NMR, absorption, and fluorescence spectra of the quinolones and in their photochemical behavior. Complexation is proposed to occur on oxygen for all of the quinolones resulting in changes in electron populations that have been probed using GAUSSIAN 86 calculations. A decrease in the energy of the oxygen nonbonding orbitals upon complexation results in a change in the configuration of the lowest singlet state from n,π^* to π,π^* upon complexation. This change results in an increase in singlet lifetime and a change in cycloaddition mechanism from triplet (stepwise) to singlet (concerted) upon complexation.

Introduction

The spectroscopy and structure of 2-quinolone (Q) are of continuing interest because of the possible existence of its tautomer, 2-hydroxyquinoline (HQ), the observation of fluorescence from the neutral and its conjugate base and acid,[2-5] and the utility of some of its derivatives as laser dyes.[6] In nonaqueous solution and in the solid state[7] Q exists in the form of the hydrogen-bonded dimer. A very large free energy of association (−8.8 kcal/mol) accounts for its limited solubility in most solvents.[8] HQ has been identified as a minor tautomer in the vapor phase, but there is no evidence for its formation upon irradiation of Q in the vapor phase or in solution.[2,3] Protonation of Q occurs on the carbonyl oxygen, resulting in a significant increase in the fluorescence quantum yield and lifetime.[4] The ground state and lowest singlet are of roughly comparable basicity.[4,5]



The photochemical behavior of Q and some of its derivatives has also been investigated. Photodimerization occurs via a triplet-state mechanism[9] to yield the anti head-to-head dimer.[10] Irradiation in the presence of both electron-rich and electron-deficient alkenes is reported to yield [2 + 2] cycloadducts, often in high preparative yield.[11-13] The absence of quenching of Q fluorescence by

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Table I. ^{1}H NMR Data for the Quinolones and Their BF_3 Complexes[a]

quinolone	solvent	H-3	H-4	4-CH_3	NCH_3
Q	CD_3CN	6.52	7.82		
Q–BF_3	CD_3CN	7.45	8.63		
Δδ		0.93	0.81		
Q–H^+	$CDCl_3$[b]	7.37	8.66		
Δδ		0.85	0.84		
MQ	$CDCl_3$	6.60		2.52	
MQ	CD_3CN	6.41		2.46	
MQ–BF_3	CD_3CN	7.33		2.77	
Δδ		0.92		0.31	
NMQ	$CDCl_3$	6.71	7.80		3.72
NMQ–BF_3	$CDCl_3$	7.31	8.53		4.12
Δδ		0.60	0.73		0.40
DMQ	$CDCl_3$	6.55		2.45	3.65
DMQ–BF_3		7.25		2.75	4.10
Δδ		0.70		0.30	0.45

[a] Chemical shifts for 0.05 M quinolone vs TMS. [b] $CDCl_3$/CF_3CO_2H mixed solvent.

Table II. ^{13}C NMR Data for the Quinolones and Their BF_3 Complexes[a]

quinolone	solvent	C-2	C-3	C-4	4-CH_3	NCH_3
Q	$CDCl_3$	164.9	121.4	138.7		
Q–H^+	$CDCl_3$[b]	162.2	118.5	149.2		
Δδ		−2.4	−3.5	9.4		
MQ	$CDCl_3$	164.3	120.4	149.2	19.0	
MQ–H^+	$CDCl_3$[b]	162.1	119.6	161.4	19.8	
Δδ		−2.2	−0.8	12.2	0.8	
NMQ	$CDCl_3$	161.8	121.2	138.5		28.9
NMQ	CD_3CN	162.0	121.8	139.5		29.4
NMQ–BF_3	CD_3CN	162.5	118.1	146.1		33.7
Δδ		0.5	−3.7	6.6		4.3
DMQ	$CD_3CN/CDCl_3$	162.0	121.1	147.1	19.0	29.2
DMQ–BF_3	$CD_3CN/CDCl_3$	161.0	117.8	155.7	19.9	33.0
Δδ		−1.0	−3.3	8.6	0.9	3.8

[a] Chemical shifts for 0.05–0.1 M quinolone vs $CDCl_3$ or TMS. [b] $CDCl_3/CF_3CO_2H$ mixed solvent.

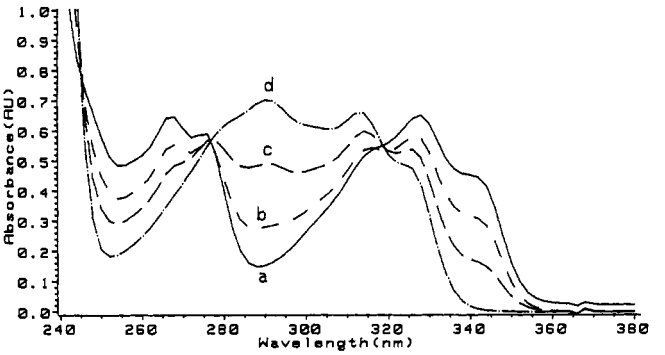

Figure 1. Absorption spectrum of 4-methyl-2-quinolone (1×10^{-4} M) in dichloromethane solution (a) and with 0.5 (b), 1.0 (c) or 2.0 (d) equiv of BF_3·OEt_2.

alkenes was taken as evidence for a triplet mechanism for cross-addition as well as dimerization.[12] The photochemical behavior of 2-quinolone is in many respects similar to that of the isoelectronic coumarin except that intersystem crossing is more efficient in the case of quinolone. Thus, triplet sensitization enhances the yield of coumarin dimers and [2 + 2] cycloadducts,[14] but is not necessary in the case of the quinolone, which undergoes efficient singlet- to triplet-state intersystem crossing.

The strong ground-state basicity and photochemical reactivity of quinolone made it an attractive target for our continuing investigation of the effects of Lewis acid complexation upon the photophysical and photochemical behavior of organic molecules.[1] We report here the results of our investigations of quinolone and three of its derivatives, 4-methyl-2-quinolone (MQ), *N*-methyl-2-quinolone (NMQ), and 1,4-dimethyl-2-quinolone (DMQ), in the absence and presence of the strong Lewis acid BF_3. Methylation on nitrogen prevents the formation of hydrogen-bonded dimers, but has little effect on photophysical or photochemical behavior. In contrast, methylation at C-4 results in the unanticipated occurrence of photoene reactions via the disproportionation of a 1,4-biradical intermediate. Complexation of all of the quinolones with BF_3 results in an increase in the singlet lifetime and the occurrence of concerted singlet-state cycloaddition reactions.

Results and Discussion

Spectra and Structure. ^{1}H and ^{13}C NMR data for the quinolones are summarized in Tables I and II along with data for their BF_3 complexes and conjugate acids. Assignments for Q are in agreement with previous studies.[15,16] Addition of 1 equiv of BF_3·OEt_2 to 0.05 M quinolone is sufficient to effect complete complexation of all of the quinolones. The use of 0.5 equiv of BF_3·OEt_2 results in the observation of signals of equal intensity for complexed and noncomplexed quinolone, indicative of slow exchange of BF_3 on the NMR time scale. Slow exchange has previously been observed for the BF_3 complexes of the cinnamamides;[1b] however, fast exchange is observed for coumarin[14] and α,β-unsaturated aldehydes, ketones, and esters.[17-19]

The BF_3-induced shifts of H-3 and H-4 for Q and MQ (Table I) are similar in sign and magnitude to those previously reported for the BF_3 complex of coumarin.[14] The chemical shifts for Q–BF_3 are similar to those for protonated Q obtained in $CDCl_3$–trifluoroacetic acid mixed solvent. The BF_3-induced shifts are intermediate in magnitude between the smaller values reported for the cinnamamides[1b] and cinnamic esters[19] and the larger values reported for simple α,β-unsaturated carbonyl compounds.[17] The BF_3-induced shifts in the ^{13}C NMR spectra (Table II) are also similar in sign, but smaller in magnitude than those for simple α,β-unsaturated carbonyl compounds.

N-Methylation has a small but noticeable effect upon the BF_3-induced NMR shifts. The shifts for H-3, H-4, and C-4 are larger for Q and MQ than for their N-methylated analogues. Evidently, part of the electron demand of the Lewis acid is met by the *N*-methyl group in NMQ and DMQ, as is the case for *N*-methylcinnamamides.[1b] However, N-alkylation does not result in an increase in the Lewis base strength of the quinolones. The observation of slow exchange for the quinolone-BF_3 complexes permits the pairwise determination of relative equilibrium constants for two quinolones present in a 1:1 ratio with 0.5 equiv of BF_3 (based on total quinolone). Comparison of NMQ with either MQ or Q indicated that the NMQ is a

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Table III. Absorption and Fluorescence Data for the Quinolones and Their BF_3 Complexes

quinolone	λ_{max}(abs),[a] nm	ϵ	λ_{max}(fl),[b] nm	Φ_f[c]	τ, ns
Q	330	7910	375	0.011	0.18
Q–BF_3	316	8830	358	0.056	1.6
MQ	328	6500	373	0.013	
MQ–BF_3	314	6590	353	0.071	
NMQ	334	5670	377		
NMQ–BF_3	318	6160	360		
DMQ	332	6710	373	0.012	0.16
DMQ–BF_3	316	7560	356	0.075	1.3

[a] Data for 0.5–1.0 × 10^{-4} M quinolone in the absence of BF_3 or in the presence of 2 equiv of BF_3–OEt_2 in dichloromethane solution. [b] Data for 10^{-5} M quinolone in deoxygenated dichloromethane solution. [c] Value relative to 7-(dimethylamino)-4-methyl-2-quinolone (Φ_f = 0.48).[6b]

weaker base by ca. a factor of 4. A decrease in Lewis base strength with N-methylation has also been observed for the cinnamamides and attributed to a steric effect on complexation.[1b] Calculations using the molecular electrostatic potential method indicate that protonation of 2-quinolones should occur in the molecular plane on the oxygen lone pair syn to NH.[5a] A similar preferred geometry for BF_3 complexation of NMQ or DMQ would be subject to nonbonded repulsion between BF_3 and the *N*-methyl group.

The long-wavelength region of the ultraviolet absorption spectrum of MQ in the absence and presence of BF_3 is shown in Figure 1, and data for the quinolones and their BF_3 complexes are summarized in Table III. Addition of BF_3 results in a blue shift of ca. 15 nm in the long-wavelength absorption band and a red shift in the second absorption band for all four quinolones. Addition of 1.5–2.0 equiv of BF_3·OEt_2 is sufficient to effect complete conversion of the quinolones (10^{-4} M in dichloromethane solution) to their Lewis acid complexes. Complete conversion of 5 × 10^{-4} M coumarin to its BF_3 complex requires saturation with BF_3 gas and cannot be achieved with 20 equiv of BF_3·OEt_2.[14] The observation that BF_3 complexation results in similar changes in the NMR and ultraviolet absorption spectra of quinolones and *N*-methylquinolones indicates that complexation does not alter the equilibrium between the quinolones and their enol tautomers.

The two long-wavelength absorption bands of the quinolones are assigned to π,π^* transitions. An n,π^* transition is calculated to occur at lower energy, but is obscured by the allowed π,π^* transitions.[3] In order to obtain further information about the nature of the frontier orbitals, GAUSSIAN 86 calculations[20,21] were conducted at the STO-3G level for Q and NMQ and for the protonated quinolones as models for their BF_3 complexes. The relative magnitudes of the HOMO and LUMO coefficients for Q and Q–H^+ are shown in Figure 2. While protonation results in changes in the orbital coefficients, most noticeably decreasing the coefficient on oxygen, it has little effect on the HOMO–LUMO energy separation, in accord with the small shift in absorption maximum upon complex formation. As previously observed for coumarin,[14] protonation results in a pronounced lowering of the energy of the n_o orbital relative to the highest occupied π orbitals. Comparison of the calculations for Q and NMQ reveals that N-methylation has little effect upon the frontier orbital energies or coefficients.

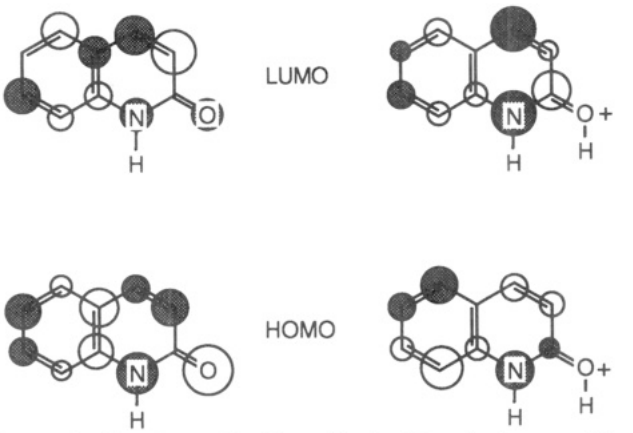


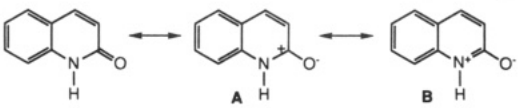
Figure 2. Frontier molecular orbitals of 2-quinolone and its conjugate acid.

Table IV. Calculated Electron Populations for Neutral and Protonated Quinolone and Coumarin[a]

quinolone	C-4	C-3	C-2	O	X	CH_3
Q	5.948	6.078	5.478	8.477	7.354	
Q–H^+	5.887	6.117	5.440	8.412	7.286	
NMQ	5.941	6.118	5.481	8.475	7.283	5.880
NMQ–H^+	5.893	6.114	5.454	8.413	7.209	5.928
C[b]	6.027	6.100	5.711	8.238	8.254	
C–H^+	5.939	6.100	5.615	8.178	8.207	

[a] Total electron populations calculated using GAUSSIAN 86 at the STO-3G level. [b] C = coumarin.

The calculated electron populations for the heterocyclic rings of quinolone, *N*-methylquinolone, and coumarin are reported in Table IV. The slightly larger populations for the carbonyl oxygen of Q vs NMQ is consistent with its greater Lewis basicity, while the significantly smaller population for coumarin is consistent with its much lower basicity. The high electron density on oxygen in the quinolones is achieved at the expense of the carbonyl carbon (and, to a lesser extent C-4 and the benzene ring) as well as nitrogen. Thus, as has recently been found for simple amides,[22] resonance structure A may be of greater



importance than the classical amide resonance structure B. N-Methylation results in a modest increase in the electron population on nitrogen and very small increases at C-2, C-3, and C-4, in accord with the small observed changes in NMR chemical shifts (Tables I and II). The electron demand of protonation is shared by N, O, C-2, and C-4, but not by C-3. Analogous changes are observed for coumarin. These changes in electron populations are consistent with the downfield shifts observed for C-4 and upfield shifts for C-3 in the ^{13}C NMR spectra of the quinolones (Table II).

Both the quinolones and their BF_3 complexes are fluorescent at room temperature in dichloromethane solution. Fluorescence emission maxima, quantum yields, and lifetimes, as determined by time-correlated single photon counting, are summarized in Table III. The short measured lifetimes of the quinolones are in agreement with

(20) (a) GAUSSIAN 86: Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Flueder, E. M.; Pople, J. A. Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA, 1984. (b) The optimized geometries differed only minimally from that reported for crystalline Q.[7]

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Table V. Preparative Yields for Photodimerization of the Quinolones

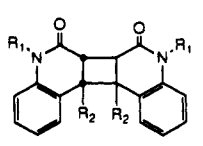
quinolone	M[a]	time,[b] h	dimer,[c] %
Q	0.21	4.0	**1a**, 84
MQ	0.53	5.5	**1b**, 86
NMQ	0.13	17	**1c**, 65
NMQ-BF_3	0.25	15	**2c**, 12
DMQ	0.12	24	**1d**, 60

[a] Concentration in deoxygenated ethanol solution. [b] Duration of irradiation with a Pyrex-filtered 400-W high-pressure mercury lamp. [c] Isolated yield.

one earlier estimate of <0.2 ns for the lifetime of NMQ in aqueous solution[23] and call into question a reported value of 2.1 ns for the lifetime of Q in aqueous solution.[4b] The fluorescence spectra of both the free and complexed quinolones bear a mirror image relationship to their absorption and fluorescence excitation spectra. The BF_3-induced blue shifts are similar in magnitude (ca. 17 nm) to those for the absorption spectra. BF_3 complexation also results in a 5- to 6-fold increase in the fluorescence quantum yield and a comparable increase in singlet lifetime.

In view of the similarity in the fluorescence rate constants ($k_f = \Phi_f \tau^{-1}$) for the quinolones and their BF_3 complexes, it appears that complexation has a much larger effect upon the nonradiative rate constant than on the absorption or fluorescence of the quinolones. A plausible explanation of the decrease in nonradiative rate constant is provided by the anticipated decrease in energy of the n_O orbital upon complexation. If the lowest singlet state of the free quinolones is in fact an n,π^* state,[3] the lifetime of the spectroscopically observed π,π^* singlet state may be determined by the rate constant for ^2S to ^1S internal conversion. A lowest n,π^* singlet state would also be expected to undergo rapid intersystem crossing to the manifold of π,π^* triplet states, providing an explanation for the efficient formation and dimerization of triplet Q (Φ ca. 0.6).[9] Complexation with BF_3 may raise the energy of the n,π^* singlet state above that of the lowest π,π^* singlet state resulting in decreased rates of internal conversion and/or intersystem crossing.

Photodimerization. Direct irradiation of Q and NMQ in solution is reported to yield the anti head-to-head dimer **1a** via a triplet-state mechanism.[9] The stereochemistry of these dimers is the same as that obtained in the triplet-sensitized photodimerization of coumarin.[14] In the 400-MHz ^1H NMR spectrum of the dimer obtained from NMQ the cyclobutane protons appear as a first-order AB quartet (J = 7.2 Hz), uniquely consistent with the assigned stereochemistry. Irradiation of MQ and DMQ also results in the formation of dimers; however, much longer irradiation times are required for conversions comparable to those obtained for Q and NMQ, in accord with an earlier report that substituents at C-3 or C-4 hinder dimerization.[12] Isolated yields of dimers obtained from preparative irradiation in ethanol solution are reported in Table V. On the basis of the similarity of their ^{13}C NMR spectra (see Experimental Section), all four quinolone dimers are assigned anti head-to-head stereochemistry.



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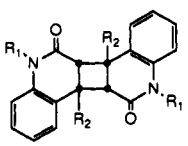
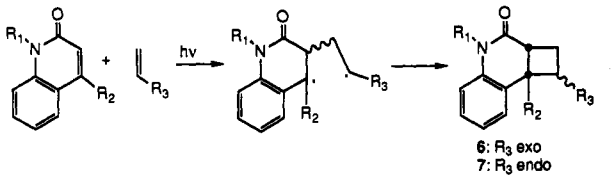


2

a: $R_1 = R_2 = H$
b: $R_1 = H, R_2 = CH_3$
c: $R_1 = CH_3, R_2 = H$
d: $R_1 = R_2 = CH_3$

(23) Teuchner, K.; Dähne, S.; Dresner, J.; Prochorow, J. *J. Lumin.* 1981, *23*, 413.

Scheme I

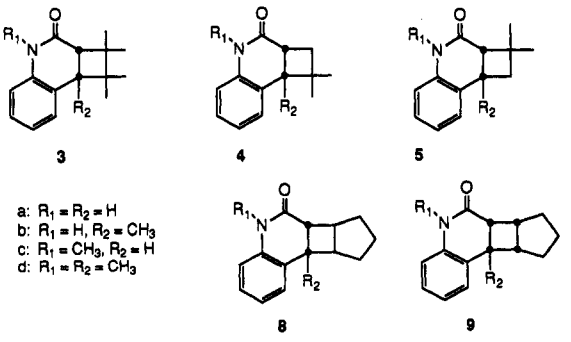


6: R_3 exo
7: R_3 endo

While C-4 alkylation hinders dimerization, N-alkylation has little effect on the initial rate or preparative yield. Thus, the quinolones that exist as hydrogen-bonded dimers (Q and MQ) vs monomers (NMQ and DMQ) undergo dimerization with comparable efficiency. Further evidence for the absence of any influence of hydrogen bonding upon photodimerization was provided by the failure of 1 equiv of benzoic acid to influence the reaction of 0.05 M Q. Since the free energy of association of the Q–benzoic acid mixed dimer is larger than that of the Q hydrogen-bonded dimer, Q should exist predominantly as the mixed dimer under these conditions.[8] While photodimerization of Q and MQ presumably involves the reaction of a triplet Q that is part of a hydrogen-bonded dimer with a ground-state Q that is part of a second hydrogen-bonded dimer, NMR analysis of the insoluble dimer that precipitates upon irradiation in ethanol shows it to contain no monomer.

Irradiation of 0.25 M NMQ with 0.5 equiv of $BF_3 \cdot OEt_2$ in dichloromethane solution results in complete inhibition of the formation of dimer **1c** and the slow formation of the syn head-to-tail dimer **2c**. The structure of the previously unreported dimer **2c** was assigned on the basis of its NMR spectra (see Experimental Section) and comparison of its ^1H NMR spectrum to that of the syn head-to-tail dimer of coumarin.[14] The cyclobutane protons in the 400-MHz ^1H NMR spectrum of **2c** appear as first-order triplets with J = 8.4 Hz, and the *N*-methyl signal is at higher field than that of dimer **1c** in both the ^1H and ^{13}C NMR spectra. The failure to observe the formation of dimer **1c** in the presence of BF_3 is a consequence of its efficient photocycloreversion to NMQ in the presence of BF_3.

Cross-Cycloaddition. The regio- and stereoselectivity of photochemical cross-cycloaddition of Q with several alkenes was previously investigated by Evanega and Fabiny.[11] In the case of 2,3-dimethyl-2-butene they report the formation of a single cis-fused cycloadduct **3a**. Addition of Q with isobutylene is reported to yield **4a**, but not its regioisomer **5a**. The monosubstituted alkenes methyl vinyl ether and acrylonitrile yielded ca. 1:1 mixture of stereoisomers **6a** and **7a**, but not their regioisomers. In the case of cyclopentene the exo and endo adducts **8a** and **9a** were formed in a 3:1 ratio. In each of these reactions dimerization of Q is competitive with cross-addition, even when the alkene is present in 10-fold excess of Q. The observation of high regioselectivity but low stereoselectivity in these cross-cycloadditions is consistent with a cycloaddition mechanism in which formation of the initial bond



3 4 5

a: $R_1 = R_2 = H$
b: $R_1 = H, R_2 = CH_3$
c: $R_1 = CH_3, R_2 = H$
d: $R_1 = R_2 = CH_3$

8 9

Table VI. Photocycloaddition of 4-Methylquinolone and Isobutylene[a]

quinolone	$(CH_3)_2C{=}CH_2$, M	time, h	4b:5b[b]
MQ	0.20	4.0	>99:1
MQ–BF_3	0.20	0.33	25:1
MQ–BF_3	0.20	4.0	3:1
MQ–BF_3	0.50	0.33	4:1
MQ–BF_3	0.50	4.0	2:1

[a] Data for deoxygenated dichloromethane solutions of 0.06 M MQ irradiated with a Pyrex-filtered 450-W high-pressure mercury lamp. [b] Isomer ratio determined by GC analysis.

Table VII. Photocycloaddition of Quinolones with Cyclopentene[a]

quinolone	8	9	10
Q	75	25	
Q–BF_3	50	50	
MQ	87	13	
MQ–BF_3	36	64	
NMQ	47	13	40
NMQ–BF_3	57	43	
DMQ	43	22	35
DMQ–BF_3	21	79	

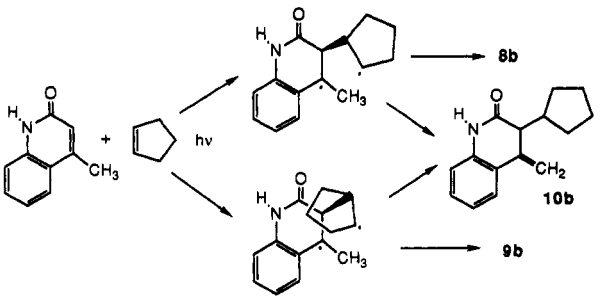
[a] Data for deoxygenated solutions of quinolone with or without 1.0 equiv of BF_3·OEt_2. Product ratios determined by analytical GC or HPLC (Q only).

occurs selectively between C-3 of triplet quinolone and the less substituted end of the alkene double bond to yield a triplet 1,4-biradical intermediate that closes nonstereoselectively to yield a mixture of stereoisomeric cyclobutanes (Scheme I).

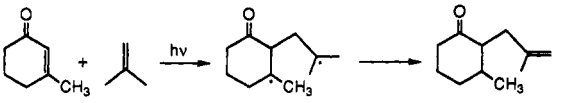
The initial objective of our reinvestigation of quinolone cycloaddition reactions was to determine the effect of BF_3 complexation upon the regio- and stereoselectivity of the cycloaddition process. The use of MQ and DMQ in our investigation was motivated both by a report that C-4 methylation hinders photodimerization but not cross-cycloaddition[12] and simplified ^1H NMR analysis of the cycloaddition products. Irradiation of DMQ with 2,3-dimethyl-2-butene in dichloromethane solution results in the formation of the cycloadduct **3d** as the major product (86% of total adduct with the remaining 14% comprised of several unidentified isomers). Irradiation of MQ with isobutylene results in essentially quantitative formation of a single adduct **4b** (Table VI). The structure of adduct **4b** is assigned on the basis of the appearance of the three cyclobutane protons as an ABX multiplet in its ^1H NMR spectrum (see Experimental Section). Thus, C-4 methylation does not significantly alter the course of cycloaddition with 2,3-dimethyl-2-butene or isobutylene.

Irradiation of MQ (or DMQ) with cyclopentene results in the formation of a mixture of exo **8b** (or **8d**) and endo **9b** (or **9d**) cycloadducts and ene products **10b** (or **10d**) along with minor amounts of quinolone photodimers. Reinvestigation of the photochemical reaction of Q with cyclopentene confirmed that exo and endo cycloadducts (**8a** and **9a**) are the exclusive products of this reaction as well as that of NMQ with cyclopentene. The relative yields of the three addition products are given in Table VII and preparative yields and spectral data in the Experimental Section. Structure assignments for the cycloadducts are based upon a comparison of ^1H NMR data with that reported by Evanega and Fabiny for **8a** and **9a** and correlation of the ^{13}C NMR data for the isomeric cycloadducts from all four quinolones. Distinction between exo vs endo isomers was based upon the appearance of (a) the cyclobutane protons derived from cyclopentene at higher field for the endo isomers, (b) the MQ and DMQ C-4 methyl protons at higher field for the exo isomers, and (c) the carbonyl carbons at higher field for the endo isomers. The relative yields of exo and endo cycloadducts and ene adduct do not change appreciably with time, indicating that all three products are primary photoproducts.

Scheme II



Scheme III



The formation of both ene and cycloadducts as primary products of the reaction of MQ and DMQ with cyclopentene is compatible with initial bonding between C-3 of triplet quinolone and cyclopentene to yield a mixture of exo and endo 1,4-biradical intermediates that can either cyclize, disproportionate via a 1,5-hydrogen atom transfer from the C-4 methyl group to the cyclopentyl radical, or revert to starting materials (Scheme II). Inspection of molecular models indicates that both the exo and endo biradicals should be capable of disproportionation. The presence of the C-4 methyl group in MQ and DMQ might be expected to hinder cyclization; however, the exo:endo ratio is not appreciably altered by N-methylation (Table VII).

While there is ample precedent to the occurrence of both cycloaddition and ene reactions via common 1,4-biradical intermediates,[24-27] the unusual feature of the present reactions is the occurrence of the ene reaction in the case of cyclopentene but not isobutylene. This result is precisely the opposite of that obtained in the reactions of 3-methylcyclohexenone in which cyclopentene yields exclusively cycloadducts and isobutylene yields exclusively the ene product when initial bonding occurs at C_α (Scheme III).[26,27] Even in the case of the reaction of DMQ with 2,3-dimethyl-2-butene a single cycloadduct accounts for 86% of all addition products, as determined by analytical GC. A second unusual feature of the reaction of the quinolone–cyclopentene-derived biradicals is that disproportionation involves the quinolone C-4 methyl group, while in the case of 3-methylcyclohexenone-derived biradicals the enone methyl group is not involved.

A plausible explanation for the different behavior of 4-methylquinolone- vs 3-methylcyclohexenone-derived biradicals is that the former are more planar and inflexible due to the presence of both a fused benzene ring and an amide functional group. The lack of conformational flexibility could account for the absence of trans-fused cycloadducts and disproportionation products with the double bond in the alkene side chain, as previously pro-

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Table VIII. Rate Constants for Quenching of Quinolone–BF_3 Fluorescence by Alkenes

quinolone	alkene	$k_q\tau$,[a] M^{-1}	10^{-9} k_q,[b] M^{-1} s^{-1}
Q–BF_3	cyclopentene	8.4	5.2
NMQ–BF_3	cyclopentene	5.8	3.6
MQ–BF_3	cyclopentene	8.4	6.4
DMQ–BF_3	cyclopentene	2.4	1.8
DMQ–BF_3	2,3-dimethyl-2-butene	13.8	10.6

[a] Slope of linear Stern–Volmer plot for fluorescence intensity vs alkene concentration in deoxygenated dichloromethane solution. [b] Calculated from $k_q\tau$ and the measured fluorescence lifetimes (Table III).

posed for the reaction of 6-methyluracil with isobutylene.[27] The order of disproportionation/combination ratios for the quinolones (cyclopentene > 2,3-dimethyl-2-butene > isobutylene) may reflect the relative amount of strain present in the cycloadducts.

Irradiation of MQ with BF_3·OEt_2 in the presence of isobutylene results in the formation of a mixture of the regioisomeric cycloadducts **4b** and **5b** and complete inhibition of MQ dimerization (Table VI). At low conversion and low isobutylene concentration **4b** is the major product; however, prolonged irradiation results in a decrease in the ratio of products **4b**:**5b** to a limiting value of ca. 2:1. Furthermore, irradiation of adduct **4b** in the presence of 1 equiv of BF_3·OEt_2 results in its conversion to the same mixture of cycloadducts. Thus, the formation of **4b** (and also possibly **5b**) is reversible in the presence of BF_3. While **4b** is the kinetically favored product, photochemical equilibrium is attained for a ca. 2:1 mixture of **4b** and **5b**.

Irradiation of all four of the quinolones with BF_3·OEt_2 in the presence of cyclopentene results in the formation of a mixture of cycloadducts **8** and **9** and complete inhibition of both dimerization and ene product formation (Table VII). The ratio of exo to endo adducts does not vary appreciably with irradiation time. Thus, either cycloaddition is irreversible or the kinetic and equilibrium product ratios are similar. In the case of the reaction of MQ with cyclopentene, variation of the cyclopentene concentration from 0.04 to 0.02 M results in an increase in the exo to endo ratio from 3.2 to 4.3. In addition to inhibiting the formation of dimers and ene products, BF_3·OEt_2 favors the formation of endo vs exo cycloadducts. This is particularly noticeable in the case of NMQ and DMQ for which cycloaddition in the presence of BF_3·OEt_2 is endo-selective (Table VII).

The fluorescence of the quinolone–BF_3 complexes, but not of the uncomplexed quinolones, is quenched by added alkene. Values of the Stern–Volmer constants obtained from the slopes of linear plots of fluorescence intensity vs alkene concentration are reported in Table VIII along with values of k_q calculated from these slopes and the measured singlet lifetimes. Values of k_q are greater than 10^9 M^{-1} s^{-1} in all cases and approach the rate of diffusion in dichloromethane solution for 2,3-dimethyl-2-butene, which is a better electron donor than is cyclopentene. While the rate constant for quenching of MQ–BF_3 by isobutylene has not been determined, the observation that 0.2 M isobutylene reduces the fluorescence by ca. 50% leads to an estimated value of $k_q \sim 1 \times 10^9$ M^{-1} s^{-1}. While quenching of quinolone–BF_3 fluorescence by alkenes is assumed to result in the formation of a singlet exciplex, no exciplex fluorescence is observed.

The observation that alkenes quench the fluorescence of quinolone–BF_3 complexes suggests that cycloaddition may occur via a concerted singlet-state process rather than the stepwise triplet-state process that occurs for the noncomplexed quinolones. This mechanistic proposal is analogous to that previously advanced for the photochemical reactions of coumarin in the absence and presence of BF_3.[14] A concerted cycloaddition reaction mechanism for quinolone–BF_3 would account for the absence of ene product formation. The failure of noncomplexed quinolone singlets to react with alkenes may be attributed in part to their short singlet lifetimes (Table IV). However, the lifetime of singlet DMQ is only a factor of 8 shorter than that of DMQ–BF_3. Thus, our failure to observe quenching of singlet DMQ by 0.1 M 2,3-dimethyl-2-butene indicates that the rate constant for quenching of singlet DMQ by this alkene must be at least 3-fold slower than quenching of DMQ–BF_3 by the same alkene.

The increased reactivity of singlet complexed vs noncomplexed quinolones with alkenes is compatible with an increase in ground- and excited-state electrophilicity upon complexation. Decreased regioselectivity both in photodimerization and cycloaddition with isobutylene may be attributed to a change in FMO coefficients upon complexation (Figure 1). Most notable is the inversion of the relative size of the LUMO C-3 and C-4 coefficients upon protonation. This change would be expected to favor initial bonding at C-4, in accord with the formation of dimer **2b** and isobutylene cycloadduct **5b** from MQ in the presence, but not in the absence of BF_3. The reversibility of photochemical cycloaddition in the presence of BF_3 is also an important factor in determining the isomer ratios obtained in these reactions.

Concluding Remarks

This investigation has revealed several interesting aspects of the photophysical and photochemical behavior of the quinolones and their BF_3 complexes. The disruption of the strong quinolone hydrogen-bonded dimer by N-methylation has surprisingly little effect upon either photophysical or photochemical behavior. The presence of a 4-methyl substituent slows the rate of photodimerization and also leads to the formation of photo-ene adducts with cyclopentane, plausibly due to a steric effect on cyclization of the 1,4-biradical intermediates formed in the reaction of the triplet 4-methylquinolones with either ground-state quinolone or alkenes. Complexation with BF_3 results in an increase in both the lifetime and reactivity of the singlet quinolones with alkenes, leading to a change in reaction mechanism from stepwise triplet to concerted singlet. The increase in lifetime is attributed to a change in the relative energies of lowest π,π^* and n,π^* singlet states and the increase in reactivity to a lowering of the frontier orbital energies upon complexation.

Experimental Section

General Methods. Melting points were determined using a Fisher-Johns melting point apparatus and are uncorrected. Ultraviolet absorption spectra were obtained using a Shimadzu UV-2100 UV–vis recording spectrophotometer or a Hewlett-Packard 8452A diode-array spectrophotometer. NMR spectra were determined (in $CDCl_3$ solution except as noted) using a Varian EM 390, a Varian XLA 400, a JEOL FX-90Q, or a JEOL FX-270 spectrometer. Fluorescence spectra were recorded on a Perkin-Elmer MFP-44A spectrometer. Fluorescence lifetimes were measured using two different single-photon counting apparatuses, one with a gated arc lamp (PTI-LS1, time resolution ca. 0.5 ns) and the other with a mode-locked dye laser (time resolution ca. 50 ps).[28] All reported lifetimes were obtained from a single-exponential fit to the fluorescence decay ($A > 0.98$). GC–mass spectra were obtained on a Shimadzu GCMS-QP-1000

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spectrometer. The light sources were a 450-W Hanovia medium-pressure mercury lamp or a Riko 400-W high-pressure mercury lamp enclosed in a water-cooled Pyrex glass well.

Irradiated solutions were analyzed either by gas chromatography (Hewlett-Packard 5890 or Shimadzu GC-8A gas chromatograph equipped with a flame-ionization detector) or HPLC (JASCO 800 series intelligent high-pressure liquid chromatograph). Cross-cycloaddition reactions were monitored using a 10 m × 0.53 mm fused silica column coated with polydimethylsiloxane, a Shimadzu Hicap CBP1-M25-025 column for GC analysis, or a JASCO SIL $C_{18}S$ column (Φ × length, 4.6 mm × 150 mm; reversed-phase type) for HPLC analysis with MeOH/H_2O (60/40) as an eluent.

Materials. 2-Quinolone (Kanto or Aldrich) and 4-methyl-2-quinolone (Aldrich) were recrystallized from ethanol prior to use. 1-Methyl-2-quinolone and 1,4-dimethyl-2-quinolone were synthesized according to literature procedures[29] and purified by sublimation or recrystallization. Cyclopentene (Aldrich) and 2,3-dimethyl-2-butene (Wiley Organics) were distilled from P_2O_5 before use. Isobutylene (Matheson) was used as received. Boron trifluoride etherate (Aldrich, redistilled) and ethanol (Nakarai, HPLC grade) were used without further purification. Dichloromethane (Mallinckrodt, spectroscopic grade) was refluxed over calcium hydride and distilled immediately prior to use.

Photodimerization. Solutions of the quinolones (0.6–2.5 mmol in 5 mL of ethanol) were irradiated in Pyrex tubes under nitrogen with a Riko or Hanovia lamp. In the case of irradiation of Q, MQ, and NMQ, the insoluble dimers were collected by filtration. In the case of DMQ, for which no precipitate was observed, the solvent was evaporated and the residue recrystallized from hexane. NMQ was also irradiated under similar conditions in the presence of 0.5 equiv of BF_3·OEt_2. After irradiation, 100 mL of dichloromethane was added and the organic solution washed with 200 mL of water and dried over $MgSO_4$. Removal of the solvent followed by column chromatography on silica gel using 2:1 hexane/ethyl acetate as elutant afforded dimer along with recovered NMQ. Irradiation times and isolated yields are summarized in Table V. Dimers were identified by analysis of their ^{13}C NMR (and ^1H NMR in the case of the dimers of NMQ) and exact mass spectra.

2-Quinolone dimer 1a: colorless crystalline solid; mp 300 °C (lit.[10c] mp 300 °C); ^{13}C NMR δ 173.9 (s), 134.1 (s), 129.9 (d), 128.4 (s), 127.1 (d), 122.5 (s), 117.9 (d), 45.0 (d), 42.9 (d).

4-Methyl-2-quinolone dimer 1b: colorless crystalline solid; mp 225–226 °C; ^{13}C NMR δ 174.0 (s), 134.6 (s), 130.2 (d), 128.8 (d), 127.4 (d), 126.0 (s), 118.8 (d), 49.2 (s), 48.1 (d), 27.8 (q); exact mass (FAB) calcd for $C_{20}H_{19}N_2O_2$ *m/e* 319.1447, found 319.1468, major fragments (rel intensity) 159 (100), 130 (79).

1-Methyl-2-quinolone dimer 1c: colorless crystalline solid; mp 220–222 °C (lit.[10d] mp 215–216 °C); ^{13}C NMR δ 169.7 (s), 139.6 (s), 128.3 (d), 127.8 (d), 123.4 (s), 123.1 (s), 115.0 (d), 44.2 (d), 43.4 (d), 29.6 (q); ^1H NMR δ 7.22–6.80 (m, 8 H), 3.72 (d, *J* = 7.2 Hz, 2 H), 3.37 (d, *J* = 7.2 Hz, 2 H), 3.18 (s, 6 H); exact mass (FAB) calcd for $C_{20}H_{19}N_2O_2$ *m/e* 319.1447, found 319.1422.

1-Methyl-2-quinolone dimer 2c: colorless crystalline solid; mp 212–215 °C; ^{13}C NMR δ 129.0 (d), 128.2 (d), 122.4 (d), 114.2 (d), 43.0 (d), 39.0 (d), 28.7 (q); ^1H NMR δ 7.07–6.49 (m, 8 H), 4.20 (t, *J* = 8.4 Hz, 2 H), 4.08 (t, *J* = 8.4 Hz, 2 H), 3.01 (s, 6 H).

1,4-Dimethyl-2-quinolone dimer 1d: colorless crystalline solid; mp 185–187 °C; ^{13}C NMR δ 168.7 (s), 139.4 (s), 128.3 (d), 128.1 (d), 126.6 (s), 122.9 (d), 115.0 (d), 47.8 (s), 46.9 (s), 29.4 (q), 27.6 (q); exact mass (FAB) calcd for $C_{22}H_{23}N_2O_2$ *m/e* 347.1760, found 347.1772.

Addition to Alkenes. Solutions of the quinolones (0.015–0.3 M) and ca. 20 equiv of alkene were irradiated in nitrogen- or argon-purged dichloromethane solution (ethanol was used in the case of Q) in the absence or presence of 1 equiv of BF_3·OEt_2 with the Pyrex-filtered output of a Riko or Hanovia lamp. The progress of reaction was monitored by GC and irradiation stopped when most of the quinolone was consumed. The solvent was then removed and the adducts isolated by column chromatography.

1,4,4,5,5,6-Hexamethyl-3,6-dihydrocyclobuta[*c*]-2-quinolone (3d): colorless crystalline solid; mp 91–92 °C; yield 64%; ^{13}C NMR δ 166.9 (s), 138.5 (s), 129.5 (s), 128.8 (d), 126.6 (d), 121.4 (d), 113.9 (d), 52.3 (d), 45.3 (s), 42.7 (s), 41.0 (s), 27.9 (q), 26.8 (q), 25.1 (q), 22.5 (q), 22.0 (q), 20.4 (q); ^1H NMR δ 7.27–6.60 (m, 4 H), 3.38 (s, 3 H, NMe), 2.92 (s, 1 H, CH), 1.30, 1.23, 1.12, 0.80, 0.78 (singlets, 3 H, Me); exact mass calcd for $C_{17}H_{23}NO$ *m/e* 257.1781, found 257.1759, major fragments (rel intensity) 174 (43), 173 (100).

5,5,6-Trimethyl-3,6-dihydrocyclobuta[*c*]-2-quinolone (4b): colorless crystalline solid; mp 57–60 °C; yield 99%; ^1H NMR δ 7.2–6.8 (m, 4 H), 2.95 (dd, 1 H), 2.34 (t, 1 H), 2.06 (dd, 1 H), 1.45 (s, 3 H), 1.18 (s, 3 H), 0.85 (s, 3 H); exact mass calcd for $C_{14}H_{17}NO$ *m/e* 215.1310, found 215.1295, major fragments (rel intensity) 159 (100), 130 (29).

4,4,6-Trimethyl-3,6-dihydrocyclobuta[*c*]-2-quinolone (5b): obtained as a mixture with **4b**; ^1H NMR δ 7.2–6.8 (m, 4 H), 2.84 (s, 1 H), 2.2 (AB quart., 2 H), 1.48 (s, 3 H), 1.3 (s, 3 H), 1.0 (s, 3 H); exact mass calcd for $C_{14}H_{17}NO$ *m/e* 215.1310, found 215.1312, major fragments (rel intensity) 159 (100), 130 (29).

3,9-Dihydrobicyclo[3.2.0]heptano[6′,7′-*c*]-2-quinolone (8a and 9a).[11b] Obtained as a mixture of isomers. **8a**: ^{13}C NMR δ 172.9 (s), 136.0 (s), 127.6 (d), 127.3 (d), 124.8 (s), 123.4 (d), 115.9 (d), 47.9 (d), 44.6 (d), 40.3 (d), 39.1 (d), 33.3 (t), 33.0 (t), 24.7 (t). **9a**: ^{13}C NMR δ 170.8 (s), 137.3 (s), 129.2 (d), 127.3 (d), 122.9 (d), 120.7 (s), 115.9 (d), 43.7 (d), 43.0 (d), 37.3 (d), 35.0 (d), 28.9 (t), 28.2 (t), 26.4 (t).

9-Methyl-3,9-dihydrobicyclo[3.2.0]heptano[6′,7′-*c*]-2-quinolone (8b and 9b). Obtained as a mixture of exo–endo isomers; mp 160–163 °C; yield 47%. **8b**: ^{13}C NMR δ 169.5 (s), 137.5 (s), 128.2 (d), 127.2 (d), 124.9 (s), 123.3 (d), 114.4 (d), 51.3 (d), 47.6 (d), 42.0 (d), 37.7 (s), 31.6 (t), 28.8 (q), 27.3 (t), 25.8 (q), 24.4 (t); ^1H NMR δ 7.3–6.9 (m, 4 H), 3.37 (s, 3 H), 2.95 (q, 1 H), 2.68 (m, 1 H), 2.60 (d, 1 H), 1.3–1.9 (m, 6 H), 1.24 (s, 3 H); exact mass calcd for $C_{15}H_{17}NO$ *m/e* 227.1311, found 227.1312, major fragments (rel intensity) 160 (12), 159 (100). **9b**: ^{13}C NMR δ 168.7 (s), 139.1 (s), 128.0 (d), 127.3 (d), 127.1 (s), 122.6 (d), 114.4 (d), 51.4 (d), 45.0 (d), 39.2 (d), 38.0 (s), 33.2 (q), 29.5 (t), 28.6 (q), 28.2 (t), 25.8 (t); ^1H NMR δ 7.3–6.9 (m, 4 H), 3.35 (s, 3 H), 3.26 (m, 1 H), 3.16 (d, 1 H), 2.75 (m, 1 H), 1.6 (s, 3 H), 1.3–1.8 (m, 6 H); exact mass calcd for $C_{15}H_{17}NO$ *m/e* 227.1311, found 227.1310, major fragments (rel intensity) 160 (11), 159 (100).

1-Methyl-3,9-dihydrobicyclo[3.2.0]heptano[6′,7′-*c*]-2-quinolone (8c and 9c). Obtained as a mixture of exo–endo isomers; mp 81–82 °C; yield 78%. **8c**: ^{13}C NMR δ 169.6 (s), 137.8 (s), 127.4 (d), 126.6 (d), 125.7 (s), 122.3 (d), 113.7 (d), 47.1 (d), 44.2 (d), 39.5 (d), 37.6 (d), 32.5 (t), 32.3 (t), 28.2 (q), 24.1 (t); ^1H NMR δ 7.25–6.85 (m, 4 H), 3.36 (s, 3 H), 3.18 (t, 1 H), 2.99 (m, 1 H), 2.90 (t, 1 H), 2.68 (s, 1 H), 1.0–1.4 (m, 6 H); exact mass calcd for $C_{15}H_{17}NO$ *m/e* 227.1311, found 227.1316, major fragments (rel intensity) 160 (12), 159 (100). **9c**: ^{13}C NMR δ 167.3 (s), 139.1 (s), 128.7 (d), 126.6 (d), 121.8 (d), 121.5 (s), 113.7 (d), 42.9 (d), 42.5 (d), 36.3 (d), 33.5 (d), 28.2 (q), 27.8 (t), 27.4 (t), 25.6 (t); ^1H NMR δ 7.25–6.85 (m, 4 H), 3.95 (dd, 1 H), 3.59 (dd, 1 H), 3.33 (s, 3 H), 3.30 (m, 1 H), 3.19 (m, 1 H), 1.0–1.6 (m, 6 H); exact mass calcd for $C_{15}H_{17}NO$ *m/e* 227.1311, found 227.1310, major fragments (rel intensity) 160 (9), 159 (100).

1,9-Dimethyl-3,9-dihydrobicyclo[3.2.0]heptano[6′,7′-*c*]-2-quinolone (8d and 9d). **8d**: ^{13}C NMR δ 172.2 (s), 135.1 (s), 131.6 (s), 127.5 (d), 127.2 (d), 123.8 (d), 116.1 (d), 51.1 (d), 47.6 (d), 42.1 (d), 38.8 (s), 31.8 (t), 27.3 (t), 25.8 (q), 24.3 (t); ^1H NMR δ 7.2–6.7 (m, 4 H), 3.0 (q, 1 H), 2.70 (t, 1 H), 2.50 (d, 1 H), 1.85 (m, 4 H), 1.5 (m, 2 H), 1.27 (s, 3 H); exact mass calcd for $C_{16}H_{19}NO$ *m/e* 241.1467, found 241.1469, major fragments (rel intensity) 174 (11), 173 (100). **9d**: ^{13}C NMR δ 171.4 (s), 136.5 (s), 127.7 (d), 127.4 (d), 125.4 (s), 123.2 (d), 116.0 (d), 51.7 (d), 45.4 (d), 39.3 (s), 39.0 (d), 33.0 (q), 29.5 (t), 28.3 (t), 25.9 (t); ^1H NMR δ 7.2–6.7 (m, 4 H), 3.28 (m, 1 H), 3.12 (d, 1 H), 2.78 (m, 1 H), 2.0 (m, 4 H), 1.62 (s, 3 H), 1.5 (m, 2 H); exact mass calcd for $C_{16}H_{19}NO$ *m/e* 241.1467, found 241.1466, major fragments (rel intensity) 174 (12), 173 (100).

3[*H*]-Cyclopentyl-4-methylidene-2-quinolone (10b): obtained as crystalline solid; mp 159–161 °C; yield 32%; ^{13}C NMR δ 173.5 (s), 141.3 (s), 135.9 (s), 129.2 (d), 124.9 (d), 123.3 (d), 123.1 (s), 115.7 (d), 113.7 (t), 55.8 (d), 42.3 (d), 30.6 (t), 30.1 (t), 24.9 (t), 24.3 (t); exact mass calcd for $C_{15}H_{17}NO$ *m/e* 227.1311, found 227.1312, major fragments (rel intensity) 160 (12), 159 (100).

1-Methyl-3[*H*]-cyclopentyl-4-methylidene-2-quinolone (10d): obtained as colorless oil; ^{13}C NMR δ 171.0 (s), 141.4 (s),

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138.7 (s), 129.0 (d), 125.1 (d), 124.9 (s), 123.0 (d), 114.4 (d), 112.8 (t), 56.3 (d), 41.7 (d), 30.5 (t), 30.1 (t), 29.4 (q), 24.8 (t), 24.1 (t); exact mass calcd for $C_{16}H_{19}NO$ m/e 241.1467, found 241.1462, major fragments (rel intensity) 174 (15), 173 (100).

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Supplementary Material Available: ^1H and ^{13}C NMR spectra of the quinolone dimers and quinolone–alkene adducts (15 pages). Ordering information is given on any current masthead page.

Pyridyl Dicyanoquinodimethane Acceptors for Electroactive Solids

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A new synthetic strategy for dicyanoquinodimethane electron acceptors is presented and used to synthesize six such compounds for the first time. The general sequence is substitution of α,α'-dicyanoxylene α anions with electrophiles followed by oxidative dehydrogenation. Unlike most previous examples, these quinodimethanes (QDs) are α substituted, rather than ring substituted; thus, the substituents increase the aspect ratio of the QDs and extend the π systems. All contain at least one pyridyl substituent at an α position, and the set includes polar, cationic, and phosphonic acid derivatives. The particular compounds were chosen for incorporation into specific types of potentially electroactive solids, although, in principle, the syntheses could accommodate a wide variety of other functional groups. The neutral QD compounds display two reversible reductions, while the cations show single, partially reversible electrochemical transitions. Syn–anti isomerism was noted for several of the QDs, and proton NMR assignments obtained by 2D COSY methods are reported.

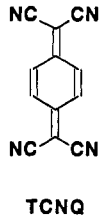
Introduction

Quinodimethanes (QDs), exemplified by tetracyanoquinodimethane (TCNQ), are among the most widely used acceptors in electron donor–acceptor complexes. These complexes may crystallize as electrically conductive[1] or magnetically interesting[2] solids. Nontrivially substituted QDs have recently been explored for the purpose of controlling the crystal packing forces in conductive[3] and ferromagnetic[2] complexes and as components in multilayer diodes prepared using Langmuir–Blodgett (LB) methods.[4] Unsubstituted[5] and amphiphilic[6] TCNQ's have been incorporated into conductive LB films by codeposition with surface-active electron donors.

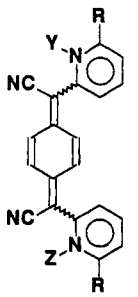
Much of the previously reported synthetic chemistry of electron-accepting QDs depends on multistep transformations of lightly substituted p-xylenes[7] or of cyclohexanediones that initially lack the α carbons.[8] The important substituents are typically placed on ring positions of the QD and are not conjugated with the QD π-electron system. The substituents would screen the QD cores from electron donors and from each other in the solid state, and the substituents considered (except for halogen or alkoxy) impart little electronic tunability to the molecules.

Here, we describe synthetic methods for functionalizing QDs at the α positions, such that the substituents may influence both the electronic behavior of the QDs and also the types of solids that might be formed from them. For the most part, the substituents are pyridine nuclei that are conjugated with the QD chromophore, so that the QD π

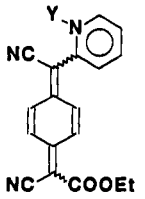
Chart I



TCNQ



1. R = H, Y = Z = lone pair (lp)
2. R = H, Y = Z = Me (+)
3. R = H, Y = Me (+), Z = lp
4. R = $PO(OEt)_2$, Y = Z = lp
5. R = $PO(OH)_2$, Y = Z = lp



6. Y = lp
7. Y = Me (+)

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