tration was against a standardized solution of HCl in 99% aqueous ethanol.

For the relatively fast runs in 80% aqueous ethanol, slow dissolution of substrate was a problem and the procedure was modified. The substrate was dissolved in 20 mL of temperature equilibrated ethanol, 5 mL of temperature equilibrated distilled water was immediately added, and, after rapid shaking, the run started.

Determination of Infinity Acid Titers. In addition to the infinity titers obtained directly from kinetic runs, others were determined by adding a small portion (usually 0.100 mL) of a freshly prepared stock solution of 1-adamantyl chloroformate in benzene to 5.00 mL of aqueous acetone or aqueous dioxane. For determinations in the presence of an added salt, the required concentration of salt was already present in the solvent. After 1 to 2 h, depending on the solvent composition, 10 mL of neutral acetone containing resorcinol blue (Lacmoid) indicator was added, and the acid developed was titrated against a standardized solution of sodium methoxide in methanol. In conjunction with the titer predicted for 100% solvolysis, the percentage of reaction involving solvolysis was calculated; averages of three experimental determinations for each mixed solvent are reported.

In a few instances the values obtained by acid titration for the partitioning between solvolysis and decomposition were checked by gravimetric analysis for free (solvolysis) and covalently bonded (decomposition) chloride. After at least 10 half-lives, the reactant solution was cooled to −15 °C and the ionic chloride was precipitated by addition of an excess of aqueous silver nitrate. The silver chloride was collected on a tared glass crucible and 30 mL of concentrated H_2SO_4 (to create a good ionizing medium[53]) was added to the filtrate. The additional silver chloride precipitated was collected on a second tared glass crucible. For example, from a reaction of 100% methanol at 24.8 °C, a total silver chloride yield of 0.307 g was calculated, and the two weights observed were 0.239 and 0.063 g, respectively.

Infrared Spectrum of Crude Product Mixtures. For reaction at 25.0 °C of 0.5 g of 1-adamantyl chloroformate in 5 mL of a pure alcohol, evolution of gas was immediately apparent. After 24 h (methanol, ethanol, *tert*-butyl alcohol) or 72 h (isopropyl alcohol), the solvent was removed by evaporation to leave a white residue. The infrared spectrum (hexane or KBr) showed no carbonyl absorption at 5.80 μm and, with the exception of the product from reaction in *tert*-butyl alcohol, no hydroxyl absorption at 3.05 μm. From the reaction of *tert*-butyl alcohol, the spectrum of the product was consistent with a mixture of 1-adamantyl chloride and 1-adamantanol and, for the other three systems, it was consistent with a mixture of 1-adamantyl chloride with the appropriate 1-adamantyl alkyl ether.

Control Experiments in *tert*-Butyl Alcohol. A 0.0471 N solution of HCl in *tert*-butyl alcohol at 25.0 °C gave an unchanged titer over at least 2 days when 1-mL aliquots were added to 10 mL of acetone prior to titration against a standardized solution of triethylamine in toluene. In contrast, when 0.052 M 1-adamantyl *tert*-butyl ether was also present in the solution, the acid titer fell in less than 16 h to a constant 52% of its value in the absence of ether. When aliquots containing the ether that had stood for in excess for 16 h were added to 50% aqueous ethanol and then allowed to stand for a further 10 h, the acid titer returned to its value in the absence of ether. Since 1-adamantyl chloride would solvolyze too slowly[16] for complete acid regeneration under these conditions, it is believed that an acid-catalyzed cleavage of 1-adamantyl *tert*-butyl ether under the reaction conditions leads to 1-adamantanol and approximately equal amounts of *tert*-butyl chloride (incorporating HCl) and isobutylene.

Product Studies by GLPC. Solutions containing about 0.006 M 1-adamantyl chloroformate in ethanol, TFE, aqueous ethanol, aqueous TFE, or TFE–ethanol were allowed to react at 25.0 °C for at least 10 half-lives. The products were directly analyzed by response-calibrated GLPC, as previously described.[23] Experiments were also carried out using 0.008 M substrate in ethanol in the presence of up to 0.08 M tetra-*n*-butylammonium bromide or tetraethylammonium chloride.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. J.B.K. thanks the Korea Science and Engineering Foundation for support during his participation in this project.

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Torsional Barriers in Quinolinone Hydroxylamine and Sulfenamide Derivatives

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The preparation of a 2-quinolinone hydroxylamine (*N*-(benzyloxy)-2(1*H*)-quinolinone) and sulfenamide derivatives of 2- and 4-quinolinone (*N*-[(2,4-dinitrophenyl)thio]-3-benzyl-4-methyl-2(1*H*)-quinolinone and *N*-[(2,4-dinitrophenyl)thio]-3-benzyl-2-methyl-4(1*H*)-quinolinone) are described. All three compounds exhibited chemical shift nonequivalence of diastereotopic benzyl methylene hydrogens, indicative of hindered rotation about the N–O or N–S bond which is slow on the NMR time scale. The torsional barriers were measured for the 2-quinolinone derivatives, while that for the 4-quinolinone sulfenamide was too large to be measured (>22 kcal/mol), indicating that in this compound the N–S chiral axis is a stable stereogenic unit on the isolation time scale.

Introduction

Barriers to torsion about the N–X bonds (X = N, O, S) in hydrazines, hydroxylamines, and sulfenamides have been the subject of a large number of investigations and have been reviewed a number of times.[2-4] Such torsional barriers confer chirality on appropriately substituted systems, and as a result, they can be detected by using NMR spectroscopy at temperatures where torsion is slow

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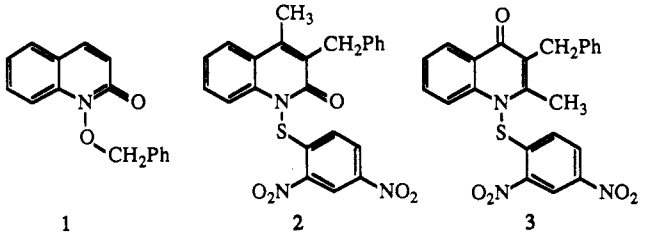
on the NMR time scale. When a prochiral probe group is incorporated into the molecule, chemical shift nonequivalence of diastereotopic hydrogens is a consequence of molecular chirality. The barrier to stereomutation can be obtained by observing coalescence of signals associated with topomerization of the diastereotopic groups in the prochiral probe group. Topomerization in these systems requires both rotation about the N–X bond and inversion of the nitrogen pyramid. In general these steps are sequential, and the mechanism can be termed rotation or torsion dominant according to the character of the transition state of the slow step. In general, the two conformational changes are sequential since the transition state for the combined process is higher in energy than either of the two transition states for the individual processes. Thus, chirality in these systems can be the consequence of either slow rotation about the N–X bond or slow inversion of pyramidal nitrogen. Accordingly, we can categorize the two types of stereomutation as I_c (inversion, chiral) and T_c (torsion, chiral) according to the slow step in the stereomutation.[1] Occasionally, in highly hindered systems, steric factors can result in exceptions to this generality. This has been well documented for topomerization in *N,N*-dialkyl-*N*-*tert*-butylamines,[5] which require torsion about C–N bonds as well as inversion of the nitrogen pyramid. Solvent, protonation, and steric effects in a highly hindered trialkylhydroxylamine series (with two tertiary substitutents at nitrogen) have also led to the postulation of a combined torsion and inversion transition state for topomerization in this series.[6]

While all of the details of the origins of these barriers are not entirely understood, it is clear that both steric and electronic effects play important roles. One electronic feature common to all of these systems is the interaction between lone pairs of electrons on adjacent heteroatoms. Simple frontier molecular orbital analyses (as well as ab initio MO calculations) demonstrate that such four-electron interactions can play a role in enhancing barriers to inversion of the nitrogen pyramid as well as enhancement of the N–X torsional barrier.[7] Compounds belonging to both I_c and T_c classes are known in all three systems (X = N, O, and S). Both kinds of processes can be responsible for the stereomutation and the topomerization that is observed by dynamic NMR spectroscopy, and coalescence behavior cannot be used to distinguish between the two classes. In some cases, the assignment of a particular molecule to one or the other of these two topomerization classes is straightforward. In other cases it may not be possible to make an unequivocal assignment of the particular category to which a particular compound belongs. In the hydroxylamines in particular there has been controversy over the assignment of compounds to the two categories.

One approach toward making such mechanistic assignments involves the construction and examination of compounds that can be unequivocally assigned to one or another class. For example, substituted aziridines and compounds in which the N–X bond is contained in a small ring belong to the I_c class. Similarly, N–X derivatives of aromatic amines and of amides can be placed in the T_c class. The barrier-lowering effect of acyl,[8] aryl,[9] and even groups that can take part in σ–π conjugation (negative hyperconjugation)[10] has been demonstrated for substituted aziridines. While the incorporation of such a conjugating group attached to nitrogen dramatically lowers the barrier to nitrogen inversion, it does not have a comparable effect on N–X torsional barriers. The similarity in the N–S torsional barriers in analogous *N*-phenyl- and *N*-isopropylsulfenamides[11] ensures that π-withdrawing groups do not have a significant barrier-lowering effect. In fact, since the barrier in the *N*-phenyl compound is somewhat higher than that in the corresponding *N*-isopropyl compound (17.8 vs 16.5 kcal/mol), it is possible that the conjugation has a slight barrier-enhancing effect. This could be due to a steric rather than electronic effect; conjugation of the nitrogen atom flattens out the nitrogen pyramid, increasing steric interactions in the torsional transition state.

Compounds in which the nitrogen atom is part of an aromatic ring are of especial interest in this regard. We can be sure in such cases that the nitrogen atom is planar, and there is no doubt that the barrier observed is not a barrier to inversion of the nitrogen pyramid. For this reason we have been interested in examining the torsional barriers in sulfenamide[12] and hydroxylamine derivatives of aromatic amines. One of our goals has been to be able to compare barriers for all three types of N–X barriers within the same aromatic system. In this paper, we report on the preparation of sulfenamide and hydroxylamine derivatives in the 2-quinolinone series, **1** and **2**, and a 4-quinolinone sulfenamide, **3**. The barriers reported here



1 **2** **3**

can be compared with barriers in quinolinone hydrazines that have been investigated fairly extensively by Atkinson.[13] This comparison allows us to comment upon a mechanistic dispute involving this system. In addition, we report NMR evidence that suggests that the barrier in the 4-quinolinone derivative **3** is large enough that the sulfenamide moiety in this system represents a stereogenic unit on the isolation time scale (i.e., it should be possible to isolate stable stereoisomers of such compounds).

There have been only a few examples of hydroxylamines in which we can unequivocally attribute nonequivalence of diastereotopic groups to the axial chirality at the oxygen–nitrogen bond and thus be confident in assigning the experimentally measured free energy of activation to the

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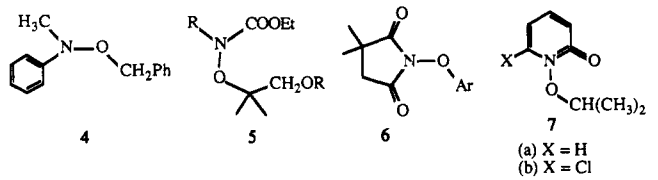
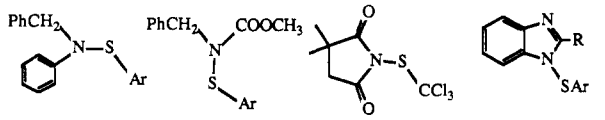
T_c process. These include an *N*-phenyl compound[14] (**4**) and *N*-acyl compounds[15,16] (**5** and **6**) as well as one case in which the nitrogen atom was part of an aromatic ring (**7**).



4 5 6 7

(a) X = H
(b) X = Cl

Sulfenamide derivatives in which the nitrogen atom is strongly conjugated also include *N*-aryl (**8**) and *N*-acyl[17] (**9** and **10**) examples as well as an aromatic system (**11**). In our study of the torsional barriers in the *N*-(arenesulfenyl)benzimidizoles, **11**, we suggested that the fairly high barriers in this system might have something to do with peri interactions of the sulfenyl moiety with the benzimidazole ring. This provided another incentive for examination of sulfenamides in the 2-quinolinone and 4-quinolinone series that are reported here.



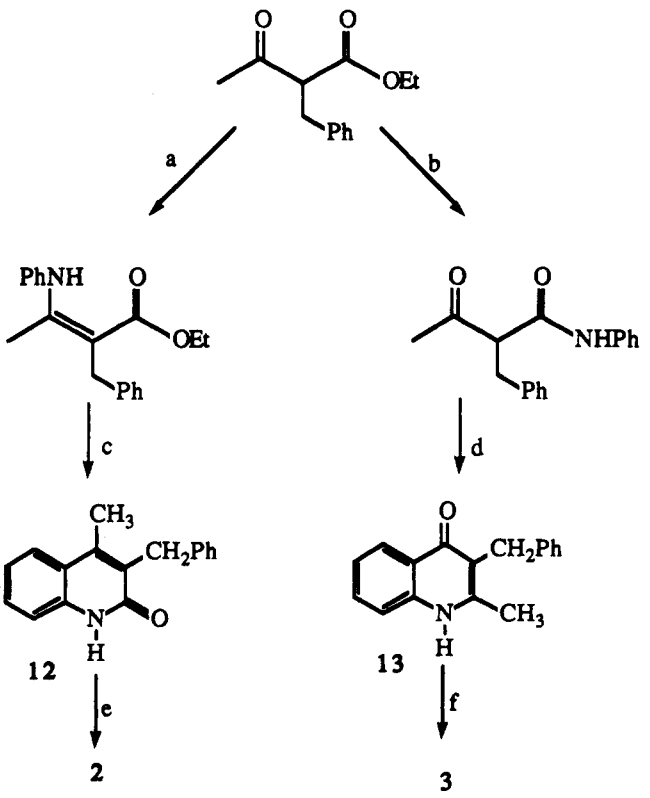
8 9 10 11

Results and Discussion

The preparation of the 2-quinolinone hydroxylamine was accomplished in a straightforward manner. Quinoline was oxidized with hydrogen peroxide in acetic acid[18] (to introduce the *N*-oxide) and then with lead tetraacetate in refluxing benzene to introduce the quinolinone oxygen.[19] The resulting hydroxamic acid (*N*-hydroxycarbostyril) was converted to **1** by deprotonation with potassium hydroxide and reaction of the anion with benzyl chloride.[20] At room temperature the NMR spectrum of **1** in chloroform-*d* features a singlet at δ 5.27 for the benzyl group, indicating that torsion about the N–O bond is rapid on the NMR time scale at this temperature. However, the singlet broadened and underwent a decoalescence as the temperature was lowered. Low-temperature NMR spectroscopy was carried out in toluene-d_8 and furnished a coalescence temperature of −55 °C. The rate constant and free energy of activation were obtained by complete lineshape analysis using a computer program that simulates the coupled exchanging AB spin system: $k_c = 25\ s^{-1}$, $\Delta G^{\ddagger} = 9.4$ kcal/mol.

The 2-quinolinone, **12**, and 4-quinolinone, **13**, used for preparation of sulfenamides **2** and **3** could both be obtained condensation of the ethyl ester of 2-benzylacetoacetic acid with aniline followed by acid-catalyzed cyclization as summarized in Scheme I. The 2-quinolinone **12** was converted into **2** by reaction with 2,4-dinitrobenzenesulfenyl chloride in the presence of DABCO in refluxing benzene. Similar conditions but with triethylamine in tetrahydrofuran were used to prepare the unsubstituted 2-quinolinone sulfenamide, **14**, which was used as a reference compound. The 4-quinolinone sulfenamide, **3**, could not be prepared by using a nitrogen base but was obtained in good yield by deprotonation of **13** with potassium hydride in tetrahydrofuran followed by treatment with the sulfenyl chloride.

Scheme I



[a] Aniline, ethanol, acetic acid, anhydrous $CaSO_4$, reflux. [b] Aniline, pyridine, xylenes, reflux. [c] Neat, 260 °C, 0.5 h. [d] H_2SO_4, H_2O, heat. [e] 2,4-Dinitrobenzenesulfenyl chloride and DABCO in refluxing benzene (or triethylamine in THF). [f] KH in THF followed by treatment with 2,4-dinitrobenzenesulfenyl chloride.

It is possible for sulfenylation of aromatic amines to occur on nitrogen or carbon; in the case of the 2-quinolinones and 4-quinolinones, sulfenylation at oxygen is also a possibility. Two pieces of evidence were obtained from NMR spectra that demonstrate that sulfenylation occurred at nitrogen. First, the resonance for H_6 of the 2,4-dinitrophenyl ring of **14** was shifted upfield to δ 7.03 (in DMSO) from δ 8.25 in the spectrum of the sulfenyl chloride (in $CDCl_3$). We have previously noted this significant upfield shift in the spectra of benzimidazole sulfenamides, **11**. It can be attributed to the sulfenamide ground-state geometry in which this proton is located over the aromatic ring and lies well within the shielding region of the ring current. Second, the doublet for the proton at position 8 in the quinolinone nucleus is shifted downfield from δ 7.30 in the 2-quinolinone to δ 7.83 in the sulfenamide, indicating a significant influence by the arenesulfenyl moiety.

The assignments of the resonances due to the ring hydrogens in the NMR spectrum of **2** were based on a homonuclear 2D (COSY) experiment. In this sulfenamide as well, the upfield shift for H_6 in the nitroaromatic ring and the downfield shift for the proton in the quinolinone nucleus peri to the N–S bond (H_8) were observed.

The assignment of the sulfenamide structure to **3** is also based on sound NMR evidence. Some of this evidence

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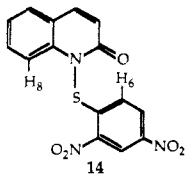
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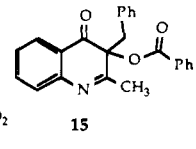
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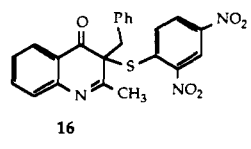

16

involves comparison with the spectra of **15**, which allowed us to rule out an analogous structure **16** for this compound. Compound **15** was obtained by treatment of the 4-quinolinone with sodium hydride followed by benzoyl peroxide. Spectral evidence, especially the ^{13}C spectrum, confirmed this structure. The key resonances were the aliphatic quaternary carbon atom, which appeared at 83.4 ppm, and the carbonyl resonance at 192.9 ppm, typical of an aryl ketone. By contrast, the ^{13}C spectrum of **3** exhibits a complete absence of resonances in the region between 115 and 35 ppm. In addition, the carbonyl resonance for **3** appears at 177.1 ppm, very close to that of the parent 4-quinolinone (175.7 ppm). This upfield shift for the quinolinone carbonyl can be attributed to the important participation of dipolar resonance structures typical of the pyridone nucleus. Comparison of the ^1H spectra of **2** and **3** also provided evidence to support the assignment. The spectrum of **3** exhibited the same downfield shift for H_8 in the quinolinone system and the upfield shift for H_6 in the nitroaromatic ring that are characteristic of the sulfenamide structure.

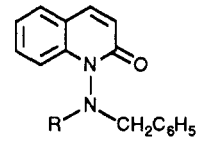
The NMR spectra of both **2** and **3** exhibited chemical shift nonequivalence for the protons attached to the prochiral methylene carbon in the prochiral benzyl group. When the temperature was raised, the spectrum of **2** in toluene-d_8 exhibited coalescence of the AB quartet due to the diastereotopic benzyl methylene protons: T_c = 67 °C, k_c = 60 s^{-1}, $\Delta G^{\ddagger}$ = 16.9 kcal/mol. By contrast, the spectrum of **3** exhibited no broadening or coalescence of the resonances due to the diastereotopic benzyl methylene protons up to 150 °C in 4:1 *o*-dichlorobenzene-d_4/toluene-d_8. Since coalescence at this temperature would correspond to a free energy of activation of about 22 kcal/mol, we can conclude that this compound would exhibit a higher barrier and should be configurationally stable at room temperature.

Comparison of the barriers in this study with those previously measured for compounds **7** and **11** can provide some insight into the steric interactions involved in the torsional transition state. We note that the barriers in sulfenamides are sensitive to steric and electronic effects. Thus comparisons between **1** and **2** cannot lead to any significant conclusion except to reinforce the observation that, in general, sulfenamide torsional barriers are higher than those in the hydroxylamine series. On the other hand, comparisons between **11** (Ar = 2,4-dinitrophenyl) should be directly comparable with those measured for compounds **2** and **3** except for differences in steric interactions.

We note that two possible diastereomeric transition states are possible for these compounds. We may term these peri and exo transition states accordingly as the sulfenyl aryl group passes close to the peri hydrogen or the substituent (alkyl in **3** and **11** and oxygen in **2**). The trend of increases in the barriers of **11** with the steric bulk of the substituent R (from 18.9 kcal/mol for R = Et to 20.7 kcal/mol when R = $CH(CH_3)Ph$) indicated that these compounds had an exo transition state and that torsion via a peri transition state would involve greater steric interactions. This conclusion was in accord with examination of molecular models. We can also conclude that the peri transition state in **2** and **3** should be even higher than that in **11**. The increase in size of the second ring will result in changes in the bond angles around the nitrogen atom. Thus (assuming idealized geometry) the CNS bond angel will decrease from about 126° to about 120° in going from the five- to the six-membered ring system. This has the effect of bringing the 2-substituent and the peri hydrogen closer to the arylthio group. Since the observed barrier for **2** is somewhat lower than those for **11**, we can conclude that both series experience an exo transition state and that passage of the nitrophenyl ring near an oxygen in **2** involves a less repulsive steric interaction than that with a methyl group in **11** even though the angles bring the two groups closer in **2**. Clearly, we can conclude that a methyl group is much larger than the quinolinone oxygen in this context. This conclusion leads directly to the prediction that if we could install an alkyl group into the 2-position of the quinolinone ring system instead of an oxygen, we might be able to significantly increase the torsional barrier. Indeed, the barrier should be considerably higher than those in **11** because of the angle changes discussed above. This conclusion is borne out by the results obtained for **3**, in which the barrier is at least 4 kcal/mol higher than that in the methyl-substituted example of **11**.

The assignment of an exo transition state for **2** leads directly to an assignment of an exo transition state for **1** since the steric factors in the two systems are comparable. The barriers observed for **7** (9.3 for R = H and 10.0 for R = Cl) are not significantly larger than that for **1** even though the *O*-alkyl group is much larger for **7**. The larger barrier observed for the chloro compound in that series is indicative of a transition state in which the isopropyl group rotates past the H rather than past the oxygen. While we cannot assign the transition state for the chloro compound, we can see that when the group here is made large enough (as in **1**) the mechanism shifts to one involving torsion past the pyridone oxygen.

Finally, our results can provide some insight into the processes involved in stereomutation of the analogous quinolinone hydrazines studied by Atkinson. That group prepared a fairly extensive series of compounds which can be exemplified by compounds **17**. Compound **17a** (R = CH_2Ph) exhibited nonequivalence of diastereotopic benzyl methylene protons up to 180 °C, the highest temperature reached. Compound **17b** (R = CH_2COOH) was resolved by classical methods and exhibited a barrier to racemization of 26.2 kcal/mol. Atkinson assigned the measured barriers in these systems to torsion about the N–N bond. The higher barriers in **17** as compared with **1** and **2** is clearly understandable in terms of our analysis. While **1** and **2** can avoid peri transition states, it is not possible for **17** to avoid interaction with the peri hydrogen as well as the quinolinone oxygen in the torsional transition state. The assignment of a T_c mechanism for these compounds was disputed by Oki,[21] who suggested that the barriers are due to slow inversion (I_c) at the exocyclic nitrogen. Although the aromaticity of the quinolinone ring system should result in planarity for the endocyclic nitrogen, we may expect that the exocyclic nitrogen is pyramidal.


17a, R = $CH_2C_6H_5$
17b, R = CH_2COOH

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However barriers of this height have never been measured for inversion of acyclic hydrazines, while the high barriers here support the expectation of high N–N torsional barriers in the comparable hydrazine system. Our results then fully support Atkinson's position and cast doubt on the position of Oki.

Experimental Section

Room-temperature ^1H and ^{13}C NMR spectra were recorded on a Nicolet QE-300 spectrometer at 300 and 75 MHz, respectively. Variable-temperature NMR spectra were recorded on a Nicolet NT 300 at 300 MHz. Coupling constants (J) are given in hertz. The temperature controller was calibrated by using either methanol or ethylene glycol in a sealed tube. IR spectra were obtained on a Nicolet 20DX FT-IR with a resolution of 2 cm^{-1}. Mass spectra were obtained on a Kratos MS80 spectrometer. Melting points were determined by using a Thomas-Hoover capillary apparatus and are uncorrected. Diethyl ether and THF were distilled under argon from sodium benzophenone ketyl before use. Hexanes and ethyl acetate were distilled from calcium hydride. Benzene was filtered before use. The 2,4-dinitrobenzenesulfenyl chloride was recrystallized from carbon tetrachloride. All other reagents were checked for purity by NMR and used as obtained from commercial sources, unless otherwise noted. Elemental formulas of all new compounds were confirmed by elemental analyses or exact mass measurements.

***N*-Hydroxycarbostyril.** Lead tetraacetate (14.2 g, wet with acetic acid) and calcium carbonate (1.5 g) were added to a solution of quinoline *N*-oxide (2.5 g, 0.017 mol) in benzene (150 mL). The mixture was heated at reflux for 2 h. Upon cooling, the reaction mixture was filtered to remove inorganic salts. The inorganic salts were washed with 100 mL of chloroform, and the combined filtrates were concentrated in vacuo. Dilute HCl (10 mL, 3%) was added to the residue, and the mixture heated to 80 °C for 30 min, resulting in the formation of a brown solid. The crude product (0.74 g, 27% yield) was recrystallized from absolute ethanol (mp 186–189 (lit.[19] mp 188–189 °C)).

***N*-(Benzyloxy)carbostyril, 1.** A solution of ethanolic potassium hydroxide was prepared by combining absolute ethanol (20 mL) and an aqueous solution of 7% potassium hydroxide (4.35 mL, 5.3 mmol) in a 50-mL flask. *N*-Hydroxycarbostyril (0.84 g, 5.2 mmol) was added, and the mixture heated (60 °C, 2 h) to effect complete solution of the hydroxamic acid. After the solution was cooled to room temperature, benzyl chloride (2 mL, 17 mmol) was added, and the solution heated at reflux for 12 h. The dark reaction mixture was concentrated in vacuo, combined with aqueous KOH (40 mL, 10%) and extracted with three portions of chloroform. The combined organic extracts were dried over anhydrous sodium sulfate and filtered, and the solvent was removed in vacuo. The crude product (mp 105–107 °C) was treated with decolorizing carbon in ether and recrystallized twice from ether/hexanes: 0.439 g, 1.75 mmol, 34%; mp 106.5–1-7.5 °C (lit.[20] mp 104–104.5 °C); ^1H NMR ($CDCl_3$) δ 7.7 (d, J = 9.6, 1 H), 7.65–7.53 (m, 4 H), 7.45–7.39 (m, 2 H), 7.25 (t, J = 7.5, 1 H), 6.80 (d, J = 9.5, 1 H), 5.29 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 157.9, 138.5, 138.2, 133.7, 130.8, 129.6, 129.0, 128.5, 128.0, 122.6, 122.4, 119.7, 112.0, 76.9.

2-Benzylacetoacetanilide. A stirred solution of ethyl 2-benzylacetoacetate (25.52 g, 0.116 mol), aniline (9.31 g, 0.100 mol), and pyridine (0.5 mL) in 150 mL of xylenes was refluxed, allowing only those components with boiling points of less than 80 °C to distill. After 1 h, 135 mL of xylenes was distilled, and the reaction mixture cooled at 0 °C for 14 h. A hexanes mixture was added and the mixture cooled to −30 °C. The off-white crude product was filtered, washed with hexanes, air dried, and used without further purification; 18.5 g, 69%, mp 108–117 °C (lit.[22] 111.5–113 °C).

3-Benzyl-4-methyl-2(1*H*)-quinolinone, 12. 2-Benzylacetoacetanilide (12.3 g, 0,046 mol) was added to a stirred solution of hot sulfuric acid (87 mL of concentrated H_2SO_4 and 44 mL of H_2O) and heated to 120 °C for 30 min, and the reaction mixture poured into 700 mL of ice water. The crude product was filtered washed with water and air dried (8.3 g, 72%). Two recrystallizations from benzene/ethanol furnished pure product, mp 239.5–241.5 °C (lit.[23] mp 238–240 °C).

3-Benzyl-2-methyl-4(1*H*)-quinolinone, 13. A mixture of freshly distilled ethyl 2-benzylacetoacetate (22.0 g, 0.1 mol), distilled aniline (9.31 g, 0.1 mol), 30 g of anhydrous calcium sulfate, 0.2 mL of glacial acetic acid, and 30 mL of absolute ethanol was heated at reflux for 5 h. The reaction mixture was filtered, the solids were washed with 50 mL of ethanol, and the combined filtrates were evaporated in vacuo. The crude ethyl β-anilino-α-benzylcrotonate was partially purified by distilling off volatile impurities 230 °C (0.01 Torr) and then cyclized to the desired product by heating at 260 °C in vacuo (0.4 Torr) for 20 min. After cooling, the crude quinolinone was recrystallized from absolute ethanol; 15.7 g, 63%, mp 290.5–294.5 °C; ^1H NMR (DMSO-d_6) δ 8.12 (d, J = 8.0, 1 H), 7.64 (t, J = 7.6, 1 H), 7.51 (d, J = 8.1, 1 H), 7.28 (t, J = 7.5, 1 H), 7.22 (d, J = 4.3, 4 H), 7.17–7.05 (m, 1 H), 3.92 (s, 2 H), 2.35 (s, 3 H); ^{13}C NMR (DMSO-d_6) δ 175.7, 147.0, 141.3, 139.2, 131.1, 128.1, 128.0, 125.4, 125.2, 123.6, 122.5, 118.2, 117.6, 29.9, 17.8; IR (KBr) 3278, 3060, 3022, 2917, 2874, 1641, 1606, 1594, 1554, 1498, 1361, 1250, 1029, 961, 853, 763, 757, 714, 698 cm^{-1}; EIMS, m/z (rel intensity) 249 (M^+, 100) 248 (89), 234 (21), 232 (13), 123 (9), 97 (11), 81 (36), 69 (69), 57 (23), 55 (26); exact mass calcd for $C_{17}H_{15}NO$ 249.1154, found 249.1148.

***N*-[(2,4-Dinitrophenyl)thio]-3-benzyl-4-methyl-2(1*H*)-quinolinone, 2.** A solution of 2,4-dinitrobenzenesulfenyl chloride (0.587 g, 2.5 mmol) in 25 mL of benzene was added dropwise with stirring to a refluxing solution of 3-benzyl-4-methyl-2(1*H*)-quinolinone (0.623 g, 2.5 mmol) and DABCO (0.28 g, 2.5 mmol) in 55 mL of benzene. The reaction was heated at reflux for 1 h after completion of addition, at which point the reaction was found to be essentially complete (TLC). The reaction mixture was filtered, and the solvent removed in vacuo. The residue which crystallized upon standing was chromatographed on silica gel (chloroform eluant) affording pure sulfenamide: 0.962 g, 81%, mp 190–192 °C; ^1H NMR (DMSO-d_6) δ 8.96 (d, 1 H), 7.24–7.25 (m, 4 H), 7.16 (m, 1 H), 7.01 (d, 1 H), 4.13 (AB qt, 2 H), 2.53 (s, 3 H); ^{13}C NMR (DMSO-d_6) δ 15.86, 32.88, 116.89, 121.25, 121.55, 123.82, 124.00, 126.21, 128.17, 128.46, 128.81, 129.23, 130.85, 139.33, 139.46, 142.64, 145.05, 145.70, 146.11.

***N*-[(2,4-Dinitrophenyl)thio]-3-benzyl-2-methyl-4(1*H*)-quinolinone, 3.** Anhydrous tetrahydrofuran (25 mL) was added via syringe to a flask charged with 3-benzyl-2-methyl-4(1*H*)-quinolinone (2.49 g, 1 mmol) and potassium hydride (0.06 g, 1.5 mmol) under a nitrogen atmosphere. After evolution of hydrogen had ceased, the flask was cooled to −78 °C and a solution of 2,4-dinitrobenzenesulfenyl chloride (0.282 g, 1.2 mmol) in THF was added dropwise. The flask was allowed to warm to room temperature over 12 h, THF removed in vacuo, and the reaction mixture partitioned between chloroform and water. The organic layer was filtered dried, the solvent removed in vacuo, and the pure sulfenamide obtained by chromatography on silica gel ($CHCl_3$ eluant) as a bright yellow solid; 0.33 g, 74%, mp 112–116 °C with slow decomposition; ^1H NMR ($CDCl_3$) δ 9.22 (d, J = 2.4, 1 H), 8.50 (dd, J = 8.0, 1.6, 1 H), 8.30 (dd, J = 9.0, 2.3, 1 H), 7.92 (d, J = 8.7, 1 H), 7.59 (ddd, J = 8.7, 7.1, 1.7, 1 H), 7.44 (dt, J = 7.5, 0.7, 1 H), 7.28–7.23 (m, 4 H), 7.21–7.14 (m, 1 H), 6.86 (d, J = 9.0, 1 H), 4.26 (d, J = 15.3, 1 H), 4.08 (d, J = 15.3, 1 H), 2.56 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 177.1, 151.4, 147.4, 146.0, 142.8, 142.5, 140.0, 133.1, 128.9, 128.5, 128.1, 127.7, 126.3, 126.1, 125.3, 125.1, 124.8, 121.8, 117.3, 32.1, 19.4.

***N*-[(2,4-Dinitrophenyl)thio]-2(1*H*)-quinolinone, 14.** A solution of 2,4-dinitrobenzenesulfenyl chloride (1.173 g, 5 mmol) in 40 mL of dry THF was added dropwise over 30 min to a solution of carbostyril (0.726 g, 5 mmol) and triethylamine (0.51 g, 5 mmol) in 100 mL of dry THF. The reaction mixture was stirred for 22 h at room temperature and filtered, and the solvent removed in vacuo as 1.7 g of crude sulfenamide (99%), yellow powder, mp 200–230 °C. A portion (1.5 g) was chromatographed on silica gel ($CHCl_3$ eluant) to give 1.05 g of yellow powder, mp 220–225 °C; ^1H NMR (DMSO-d_6) δ 8.95 (d, 1 H), 8.35 (dd, 1 H), 8.13 (d, 1 H), 7.83 (m, 2 H), 7.53 (m, 1 H), 7.34 (m, 1 H), 7.05 (d, 1 H), 6.8 (d, 1 H); ^{13}C NMR (DMSO-d_6) δ 161.8, 145.8, 145.1, 142.7, 142.2,

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141.0, 131.5, 129.5, 128.9, 125.0, 123.8, 121.8, 120.8, 116.8.

3-(Benzoyloxy)-3-benzyl-2-methyl-4-quinolinone, 15. Anhydrous THF (40 mL) was added to a flame-dried flask charged with NaH (0.144 g, 5.8 mmol) and 3-benzyl-2-methyl-4(1*H*)-quinolinone (1.00 g, 4.0 mmol). After evolution of hydrogen had ceased, the flask and its contents were cooled to -78 °C, and a solution of benzoyl peroxide (1.16 g, 4.8 mmol) in 20 mL of THF was slowly added. The flask was kept at -78 °C for 12 h and then allowed to warm slowly to room temperature over 3 h. The solvent was removed in vacuo, the residue partitioned between chloroform and water, and the aqueous layer washed with chloroform. The combined organic layers were dried, and the solvent was removed in vacuo, leaving an orange oil, which was chromatographed on silica gel (hexanes/ethyl acetate eluant) to give a yellowish white solid, 0.64 g, 43%. A small amount was purified by HPLC to provide a sample for NMR and EIMS; ^{1}H NMR ($CDCl_3$) δ 8.1k (d, J = 7.8, 2 H), 7.92 (dd, J = 7.6, 1.5, 1 H), 7.66-7.58 (m, 2 H), 7.52 (t, J = 7.6, 2 H), 7.43 (d, J = 7.6, 1 H), 7.32 (dd, J = 7.5, 1.9, 1 H), 7.22-7.14 (m, 5 H), 3.38 (d, J = 13.4, 1 H), 3.30 (d, J = 13.5, 1 H), 2.10 (s, 3 H); ^{13}C δ 192.9, 174.3, 165.6, 146.2, 136.0, 133.9, 131.8, 130.3, 130.2, 130.1, 128.6, 128.3, 128.1, 127.8, 127.6, 126.0, 123.4, 83.4, 42.5, 22.0; EIMS, m/z (rel intensity) 369 (M^+, 31), 264 (14), 251 (29), 105 (100), 91 (30), 77 (27), 51 (6), 28 (16); exact mass calcd for $C_{24}H_{19}NO_3$ 369.1364, found 369.1359.

Registry No. 1, 5280-06-8; 2, 124443-74-9; 3, 124443-75-0; 12, 124443-77-2; 13, 124443-78-3; 14, 124443-79-4; 15, 124443-80-7; 16, 124443-81-8; $H_3CCOCH(CH_2Ph)CO_2Et$, 620-79-1; $H_3CC(NHPh)=C(CH_2Ph)CO_2Et$, 124443-76-1; $H_3CCOCH(CH_2Ph)CONHPh$, 528-76-7; carbostyril, 493-62-9.

Supplementary Material Available: Low-temperature ^{1}H NMR spectrum of 1, room-temperature ^{1}H NMR spectrum of carbostyril with assignments, room-temperature ^{1}H NMR spectrum of 14 with assignments, room-temperature ^{1}H NMR spectrum of 2 with assignments, COSY ^{1}H NMR spectrum of 2 with assignments, and room-temperature ^{1}H NMR spectrum of 3 (6 pages). Ordering information is given on any current masthead page.

Heteroatom Effects on the Photophysical Properties and Conformational Equilibrium of *trans*-1-Phenyl-2-(2-quinoxalinyl)ethene

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The absorption and fluorescence spectra of conformationally restricted *trans*-1-phenyl-2-(3-methyl-2-quinoxalinyl)ethene (MQxPE) match the long-wavelength spectral component of *trans*-1-phenyl-2-(2-quinoxalinyl)ethene (QxPE) which exists in a conformational equilibrium. MM2 calculations predicted four global energy minima for QxPE. One set of enantiomeric geometries with the quinoxaline ring coplanar with the molecular plane has a lower energy (about 0.8 kcal/mol lower) than the other rotamers which have the quinoxaline ring twisted out of the molecular plane (-9.2 or +9.2). A large solvent effect on the fluorescence spectra was observed which can be attributed to the proximity effect caused by the vibronic interaction between the lowest (π,π^*) and (n,π^*) states.

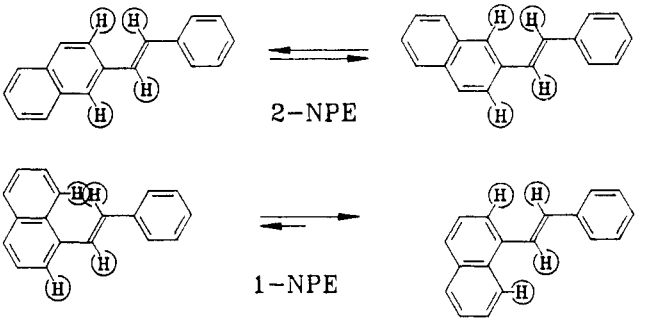
Introduction

The emission spectroscopy of *trans*-1,2-diarylethenes in solution has been the subject of great interest in the past few years since these molecules exist in equilibria between the relatively unhindered (quasi-planar) conformers around the quasi-single bond connecting the aromatic group and ethylenic carbon.[1] Dramatic changes in the emission properties (spectral shape, quantum yield, and lifetime) of the *trans*-1,2-diarylethenes upon variation of excitation wavelength were observed and attributed to these conformational equilibria.[1b-d]

The detection of ground-state rotational conformers by emission spectroscopy is based on the hypothesis that the excited-state conformers do not interconvert during their lifetimes, in accord with the so-called "principle of nonequilibration of excited rotamers (NEER)", first proposed by Havinga and co-workers[2] in order to rationalize the photochemical behavior of conjugated trienes. The bond order of the quasi-single bond between the aromatic ring and ethylenic carbon in *trans*-1,2-diarylethenes is remarkably enhanced upon excitation, such that conformational changes which occur freely in the ground state are rendered very difficult, leading to noninterconverting excited molecules. Since each of the ground-state conformers in equilibrium has its own distinctive absorption characteristics, different excitation wavelengths can lead to different compositions of conformers in the excited state and consequently to wavelength-dependent emission behavior.[1]

Calculations of the ground-state potential curves for internal rotation about the quasi-single bonds[3] have dem-

Scheme I



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