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Photochemical generation of thiophene analogs of 9-fluorenyl cations

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The 9-fluorenyl cation is a member of the 4N Hückel antiaromatic series of intermediates, first observed by time-resolved spectroscopy on UV photo-excitation of 9-fluorenol. Thiophene analogs of 9-fluorenol in which one of the annelated benzene rings is replaced by a thiophene were prepared in three regioisomeric forms, and subjected to preparative and laser flash photolysis. Photoproduct studies in methanol indicated products derived from the corresponding fluorenyl cations and radical intermediates. Time-resolved spectroscopy showed transients which were assigned to the corresponding cations as evident from methanol quenching. The lifetimes and methanol quenching rates of these transients were compared with those of parent fluorenyl cation, and were found to be about two orders of magnitude more stable than the latter. On the other hand thermodynamic stabilities obtained from theoretical calculations based on isodesmic reactions of the open form cations, and NICS indicate that two of these ions (2 and 4) are less stable than 9-fluorenyl cation, whereas the "side" isomer 3 is slightly more stable. Copyright © 2010 John Wiley & Sons, Ltd.

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INTRODUCTION

The concept of antiaromaticity to describe the destabilization of cyclic π -systems has been in existence for more than four decades,^[1,2] and has been extended to account for the properties of isoelectronic ionic and radical intermediates.^[3]

The 9-fluorenyl cation 1 is a member of the general class of cyclic 4N π -systems exhibiting destabilizing properties. Whereas these intermediates have been postulated in solvolysis reactions, their direct observation by classical low temperature NMR detection from alcohol precursors in superacids has never been realized. The direct observation of the 9-fluorenyl cation as a short-lived transient ($\tau < 20 \times 10^{-12} \, \text{s}$ in methanol) by laser flash excitation of 9-fluorenol in neutral solutions was first reported in 1989.^[4] The lifetime of this species can be extended in polar non-nucleophilic solvents such as 1,1,1-trifluoroethanol or 1,1,1,3,3,3-hexafluoroisopropanol.^[5] The pK_{R+} value for 9-fluorenyl cation is 4.2 less than the benzhydryl cation indicating the destabilization of the former relative to the open form.^[6] This factor is also borne out by calculated destabilization energies of 8-10 kcal/mol relative to benzhydryl cation for isodesmic reactions involving hydride or hydroxide ion transfer.^[6,7,8] This is equivalent to a rate retardation of a factor of 10⁶ to 10⁷ at 25 °C for 9-fluorenyl cation formation in solvolysis reactions compared to the benzhydryl system.

The π -isoelectronic structure of thiophene with benzene suggests similar cations could be generated from their alcohol precursors upon replacing one or both benzene rings of 9-fluorenyl cation. However the lower symmetry of this heterocycle leads to formation of three possible regioisomers upon replacement of a single benzene with a thiophene-ring.



These regioisomeric cations are denoted as the up-**2**, side-**3**, and the down-**4** species. Thiophene exhibits enhanced nucleophilicity compared to benzene. This is reflected in the aromatic stabilization energies (22.4 kcal/mol for thiophene *vs.* 26.7 kcal/ mol for benzene)^[9] and the proton affinities (196.5 kcal/mol for thiophene *vs.* 181.3 kcal/mol for benzene).^[10] Thus replacement of one or both of the phenyl rings in the 9-fluorenyl cation with a

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thiophenyl ring might be expected to lead to enhanced thermodynamic stability of the 12π annulene system. Conversely, the presence of sulfur in the thiophene derivatives would be expected to confer a decreased reactivity at the nucleofugal carbon of ions **2–4** relative to fluorenyl cation **1** as a result of the enhanced nucleophilicity of thiophene relative to benzene. Thus, it was of interest to compare relative thermodynamic and kinetic stabilities between these cations. Given that the fluorenyl cation can be generated from electronic excitation of 9-fluorenol, the likely precursors necessary for the generation of cations **2–4** would be the corresponding indenothiophenols **5–7**.



RESULTS

Synthesis of the fluorenol precursors

The preparation of the "up-" isomer **5** followed the synthetic sequence outlined in Scheme 1.

Reaction conditions: a. Pd(PPh₃)₄/C₆H₆ (98%); b. LiAlH₄/THF (42%); c.PPA, 120 $^{\circ}$ C (69%); d.NBS/CCl₄, *hv*; e. AgNO₃/acetone/H₂O (44%).

The synthesis of methyl 2-(3-thienyl)benzoate (8) was accomplished using a Suzuki coupling reaction between methyl 2-iodobenzoate (1.5 eq.) and thiophene-2-boronic acid.^[11] The yield for this reaction was quantitative as evident from the NMR spectrum of the crude reaction mixture. Alcohol **9** was obtained from LAH reduction of ester **8** in 42% yield. The proton NMR spectrum of alcohol **9** showed peaks in the aromatic region that was shifted upfield relative to the starting material, along with a 2H singlet at δ 4.7 ppm for the methylene hydrogens and 1H

singlet at δ 1.8 ppm for the alcohol proton. Polyphosphoric acid (PPA) was used to cyclize the central 5-membered ring, forming 8H-indeno[2,1-b]thiophene (**10**) in 69% yield. The product was identified by ¹H-NMR spectroscopy. The ¹³C-NMR spectrum shows the expected ten aromatic carbon signals with 4 weak signals associated with the quaternary carbons.

The preparation of up-**5** involved a two-step reaction using NBS bromination of **10** in carbon tetrachloride followed by hydrolysis to the alcohol with aqueous silver nitrate. The ¹H-NMR spectrum of up-**5** was consistent with the structure showing a 6:1 integration of the aromatic to aliphatic protons signals. The C-8 proton appears at δ 5.4 ppm with the alcohol peak at 2.3 ppm, both appearing as doublets. The ¹³C-NMR spectrum shows the expected ten aromatic signals at δ 149.5, 146.8, 146.7, 137.5, 131.5, 131.0, 128.9, 125.8, 124.8, 119.3, 118.7 ppm and one aliphatic carbon signal at δ 72.6 ppm. The mass spectrum shows the molecular ion at m/z = 188 with a fragment ion corresponding to loss of hydroxide at m/z = 171.

Preparation of down-7 followed the same protocol as used for the synthesis of 5, with the use of 2-thiophene boronic acid in place of 3-thiophene boronic acid in the Suzuki coupling (Scheme 2).

Reaction conditions: a. Pd(PPh₃)₄/C₆H₆ (66%); b. LiAlH₄/THF (75%); c.PPA, 120 $^{\circ}$ C (17%); d.NBS/CCl₄, *hv*; e. AgNO₃/acetone/H₂O (39%).

Ester **11** was obtained in 66% yield. The ¹H-NMR spectrum is consistent with the structure showing an integration of 7:3 of the aromatic to the aliphatic methyl proton signals (δ 3.7 ppm) of the ester. Reduction of **11** with lithium aluminum hydride in THF forms the corresponding alcohol **12** in 75% yield. Dehydrative cyclization of **12** was carried out by the addition of a CH₂Cl₂ solution of **12** to neat pre-heated PPA (120 °C). The reaction proceeded in significantly lower yield (17%) as compared to that of **9**, due presumably to the lower nucleophilicity at C-3 compared to C-2 of the thiophene ring. The remainder of the isolated organic material consisted of some unreacted material along with unidentified side products. The ¹H-NMR spectrum is consistent with the structure. The same cyclization was attempted on the methyl ester of this compound without success.

The last step of the synthesis of the down alcohol **7** was performed in the same manner as with **5**. However in this case



Scheme 1. Synthetic pathway for the preparation of 8H-indeno[2,1-b]thiophen-8-ol (5).



Scheme 2. Synthetic scheme for the preparation of 4H-indeno[1,2-b]thiophen-4-ol (down-7).

roughly half of the product obtained after treatment of the bromide with silver nitrate was the target alcohol and the other half was the corresponding ketone. The oxidation likely occurred due to the use of excess silver nitrate. Nevertheless, the ketone could be easily reduced with sodium borohydride in methanol to give additional amounts of alcohol **7**. The overall yield was 39%. The ¹H-NMR spectrum of **7** is consistent with its proposed structure, exhibiting aromatic signals integrating to six protons, with the C-4 proton appearing at δ 5.4 ppm and the alcohol proton at δ 3.85 ppm. The ¹³C-NMR spectrum shows the expected ten aromatic carbon signals at δ 150.6, 149.0, 143.6, 136.8, 128.8, 127.8, 126.0, 124.8, 122.7, 118.8 ppm as well as the C-4 aliphatic carbon signal at δ 72.1 ppm. The mass spectrum shows the molecular ion at *m*/*z* = 188 with loss of hydroxide at *m*/*z* = 171.

A slightly different approach was undertaken for the preparation of the middle alcohol precursor **6**. Using 3,4-dibromothiophene, an attempt was made to introduce the electrophilic moiety for the cyclization reaction on the thiophene ring and then carry out the Suzuki coupling to a phenyl ring. This proved inefficient. The preferred pathway involved initial Suzuki coupling to phenyl boronic acid followed by carboxylation (Scheme 3).

The initial Suzuki coupling was done using a 1:1 stoichiometric molar ratio in order to maximize the yield of the mono-coupled product. The product yield was 68%. The ¹H-NMR spectrum was consistent with the structure. Carboxylation of 3-bromo-4-phenylthiophene was carried out by lithiation with *n*-butyl lithium followed by addition of gaseous CO₂. The yield was reasonably high (87%), and 14 was obtained in sufficient purity that column chromatography was not necessary. The integration ratios in the ¹H-NMR spectrum were consistent with its molecular structure. The carboxylic acid proton appeared unusually upfield at δ 5.2. Direct cyclization of acid **14** could be effected in hot (200 °C) PPA. The ¹H-NMR spectrum is consistent with ketone 15, and coupling constants were used to distinguish between protons on the thiophene ring and those on the phenyl ring. Long range coupling of about 2 Hz was observed for the protons on the thiophene ring. The reduction step to alcohol 6 was effected with sodium borohydride. The yield was near quantitative (96%) without the need for purification by chromatography. The ¹H-NMR spectrum of **6** was consistent with its structure. The same thiophene long range coupling constants were observed as with 8H-indeno[1,2-c]thiophene. The C-8 proton appears at δ 5.5 ppm with the alcohol proton



Scheme 3. Synthesis of 8H-indeno[1,2-c]thiophen-8-ol (6).



Scheme 4. Photoproducts from irradiation of alcohols 5, 6, and 7.

appearing at δ 2.2 ppm both as doublets (J = 9 Hz). The ¹³C-NMR spectrum showed the expected ten aromatic carbon signals with the benzylic C-8 carbon at δ 70.3 ppm. The mass spectrum is similar to the previous two isomers showing a molecular ion at m/z = 188 and a peak at m/z = 171 corresponding to loss of hydroxide.

Photoproduct studies

Solutions of alcohols 5, 6 and 7 in methanol $(8 \times 10^{-3} \text{ M})$ were irradiated for a common time period and the products were then isolated. The intermediacy of the carbocations was established by the formation of the methyl ether photosolvolysis products. Other products were formed from corresponding radical intermediates. These included the corresponding fluorene analogs 10, 19, and 13, respectively, from hydrogen atom abstraction, and the fluorenone analogs 17, 15, and 21 from radical disproportionation or oxidation pathways (Scheme 4).^[12] The structural assignments of all photoproducts were based on comparison with samples prepared independently. The methanolysis products 16, 18, and 20 were prepared from methanol solvolysis of the corresponding benzylic bromides prepared from fluorenes 10, 19, and 13, respectively. Small amounts (<5%) of the bifluorenyl analogs were observed from alcohols 5 and 6 which were not unequivocally characterized. Alcohol 7 gave the smallest amount of photomethanolysis product, with radical-derived products being the most predominant. Table 1

lists the isolated yields of the major identified products from these experiments.

Laser flash photolysis

Laser flash photolysis experiments were carried out using a KrF excimer laser for excitation (248 nm, \sim 25 ns, \sim 100 mJ) and deoxygenated 0.15–0.20 mM solutions of alcohols **5**, **6**, and **7** in HFIP. Transient spectra were recorded using a flow system, while rate constants for methanol (MeOH) quenching were measured using a series of static samples containing different concentrations of the added substrate. Experiments with 9-fluorenol in HFIP were carried out using a series of static samples.

8H-Indeno[2,1-b]thiophen-8-ol (5)

Laser photolysis of **5** gave rise to two detectable transient species with overlapping absorption spectra (see Fig. 1a). The dominant absorption exhibited $\lambda_{max} \sim 500$ nm and lifetime $\tau \sim 20 \ \mu$ s, while the weaker one was much longer lived ($\tau = 385-740 \ \mu$ s) and exhibited $\lambda_{max} \sim 470$ nm. Addition of MeOH to the solution caused a shortening of the lifetime of the 500 nm species and a reduction in the intensity of the long-lived (470 nm) component of the decay; the latter was eliminated completely in the presence of 1.94 M MeOH. This behavior suggests that the 470 nm species is a product of reaction of the 500 nm species, its formation being suppressed in the presence of a substrate (i.e.

Table 1. Photoproduct distribution for thiophene fluorenol analogs 5–7 ^a (1 h irradiation)							
Alcohol	Methanolysis products (%)	Fluorene analog (%)	Ketone (%)	Unreacted alcohol (%)			
5	16 (13)	10 (14)	17 (28)	(35)			
6	18 (30)	19 (35)	15 (12)	(17)			
7	20 (2)	13 (27)	21 (69)	(1)			
^a Yields are based on ¹ H-NMR integrations with pure reference standards.							



Figure 1. (a) Time-resolved UV–Vis absorption spectra recorded by laser flash photolysis of a deoxygenated 0.2 mM solution of **5** in HFIP, 0.32–0.96 μ s (\bigcirc), 27.5–28.8 μ s (\square), and 155.5–156.8 μ s (Δ) after excitation. (b) Plot of the pseudo-first order rate constant for decay of the 500 nm species vs. [MeOH]; the solid line is the fit of the data to Eqn. 1.

MeOH) that reacts competitively with its direct precursor. The short-lived species is assigned to carbocation **2**; the identity of the longer-lived transient is more difficult to assign, but may be a dimeric cationic species derived from electrophilic attack of the primary formed cation with **5**. Such bimolecular reactions have been reported for the 9-fluorenyl cation **1**.^[13,14]

A plot of the pseudo-first order rate constant for decay of the 500 nm species (k_{decay}) vs. [MeOH] (Fig. 1b) exhibited positive curvature, indicating that the species reacts with the alcohol via a mechanism in which the order with respect to MeOH is higher than one. The data were thus fit to the quadratic expression of Eqn. 1, where k_0 is the pseudo-first order decay rate constant in the absence of added substrate, and k_1 and k_2 are overall second-and third-order rate coefficients, respectively, for reaction of the species with MeOH; a reasonable fit of the data required that k_0 and k_1 be constrained to positive values. The analysis afforded k_0

and k_1 values equal to zero within the estimated error limits, and a k_2 value of $k_2 = (4.8 \pm 1.9) \times 10^5 \,\text{M}^{-2} \,\text{s}^{-1}$, where the error is expressed as twice the standard deviation from the non-linear least squares fit.

$$k_{\text{decay}} = k_0 + k_1 [\text{MeOH}] + k_2 [\text{MeOH}]^2$$
(1)

8H-Indeno[1,2-c]thiophen-8-ol (6)

Two transients with overlapping absorption spectra were also observed for this isomer (Fig. 2a): a short-lived species exhibiting $\lambda_{max} \sim 500$ nm and lifetime $\tau \sim 15 \ \mu$ s, which is formed with the laser pulse and is assigned to carbocation **3**, and a longer-lived transient with $\lambda_{max} \sim 460$ nm and $\tau \sim 140 \ \mu$ s. The longer-lived transient absorption (or at least part of it) shows a discrete growth that occurs over a similar timescale as the decay of the



Figure 2. (a) Time-resolved UV/Vis absorption spectra recorded by laser flash photolysis of a deoxygenated 0.15 mM solution of **6** in HFIP, 0.32–0.64 μ s (\bigcirc), 30.7–31.7 μ s (\bigcirc), and 107.5–108.5 μ s (\square) after excitation. (b) Plot of the pseudo-first order rate constant for decay of the 500 nm species (monitored at 520 nm) vs. [MeOH]; the solid line is the fit of the data to Eqn. 1.

first-formed transient, suggesting that it is a product of the latter species. However, the absorption was not completely eliminated upon addition of up to 2 M MeOH; a trace recorded at 460 nm in the presence of 2 M MeOH was roughly 30% as intense as in the absence of the alcohol, and exhibited $\tau = 20 \,\mu$ s. This suggests that the longer-lived transient absorption consists of contributions from at least two species, one whose formation is quenched by added MeOH, and one that is most likely formed along with **3** during the laser pulse and whose lifetime is relatively insensitive to the presence of added MeOH.

A plot of k_{decay} vs. [MeOH] for the short-lived 500 nm species again exhibited positive curvature (see Fig. 2b), but the fit to Eqn. 1 was essentially quantitative and afforded a k_1 value equal to zero, consistent with a pure second-order dependence on MeOH concentration. The analysis afforded $k_2 = (4.6 \pm 0.5) \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$, where the error is again expressed as $\pm 2\sigma$.

4H-Indeno[1,2-b]thiophen-4-ol (7)

Laser photolysis of alcohol **7** resulted in the formation of two transients with well-separated absorption spectra and markedly different temporal behaviors (Fig. 3a). The shorter-lived absorption, tentatively assigned to carbocation **4**, was formed with the laser pulse and exhibits $\lambda_{max} = 480 \text{ nm}$ ($\tau = 8 \mu s$). The second species ($\lambda_{max} = 360 \text{ nm}$) grew in after the laser pulse over a similar timescale as the decay of the 480 nm absorption, again suggesting it is a product of the first-formed transient. Addition of MeOH led to discrete reductions in the lifetime of the 480 nm species, and a plot of k_{decay} vs. [MeOH] again showed positive curvature. The fit to Eqn. 1 was relatively poor, but afforded $k_2 = (4.5 \pm 3.5) \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$ and k_0 and k_1 values indistinguishable from zero. The effect of added MeOH on the 360 nm transient absorption was not determined.

9-Fluorenol

Laser flash photolysis of static solutions of 9-fluorenol in HFIP afforded strong transient absorptions at 500 nm, which decayed



Figure 4. Plot of the pseudo-first order rate constant for decay of the 9-fluorenyl cation in deoxygenated HFIP at 25 °C vs. [MeOH]. The solid line is the non-linear least squares fit of the data to Eqn. 1.

with good pseudo-first order kinetics and exhibited $\tau \sim 10 \,\mu s$. This is in good agreement with the results of McClelland *et al.*,^[5] who assigned the species obtained under these conditions to the 9-fluorenyl cation ($\lambda_{max} = 515 \,\text{nm}$). Addition of MeOH resulted in a shortening of the transient lifetime, and a plot of k_{decay} vs. [MeOH] exhibited positive curvature over the 0–0.3 M concentration range in added MeOH (see Fig. 4). Analysis of the data according to Eqn. 1 afforded k_0 and k_1 values indistinguishable from zero within experimental error, and $k_2 = (4.8 \pm 3.6) \times 10^7 \,\text{M}^{-2} \,\text{s}^{-1}$.

Figure 5 shows plots of k_{decay} vs. [MeOH]² for all four of the carbocations studied in this work, along with the results of linear least squares analysis of the data according to Eqn. 2. As can be seen in Fig. 5a, the plots for **2–4** all show very good linearity



Figure 3. (a) Time-resolved UV/Vis absorption spectra recorded by laser flash photolysis of a deoxygenated 0.17 mM solution of **7** in HFIP, 0.16–0.64 μ s \diamond and 37.8–38.2 μ s (\Box) after excitation. (b) Plot of the pseudo-first order rate constant for decay of the 500 nm species (monitored at 520 nm) vs. [MeOH]; the solid line is the non-linear least squares fit of the data to Eqn. 1.



Figure 5. Plots of the pseudo-first order rate constants for decay of (a) cations **2–4** and (b) the 9-fluorenyl cation (**1**) in deoxygenated HFIP at 25 °C vs. $[MeOH]^2$. The solid lines are the linear least squares fits of the data for $[MeOH]^2 \le 2.0$ M to Eqn. 2.

over the 0–2.0 M concentration range in added MeOH. The corresponding k_2 values obtained from least squares analysis of the data over this concentration range are listed in Table 2

$$k_{\text{decay}} = k_0 + k_2 [\text{MeOH}]^2 \tag{2}$$

Theoretical calculations of cation stabilities

In order to assess the relative stabilities of cations **1–4**, energies for the isodesmic reactions for hydride transfer between the fluorene analogs and the corresponding benzhydryl analogs (Scheme 5) were computed at the B3LYP/6-311G^{**} level of theory.

The computed energy for the hydride transfer between fluorene and benzhydryl cation agrees well with previous computations at lower levels of theory.^[8] It can be seen that thiophene cations **4** and **2** are thermodynamically less stable than **1** relative to the open form with respect to the hydride transfer isodesmic reactions depicted in Scheme 3. On the other hand, cation **3** is calculated to be more stable relative to the corresponding acyclic cation than 9-fluorenyl. Between the isomeric cations **2–4**, side- **3** is more stable than up-**2** and down-**3** by 1.6 and 5.2 kcal/mol, respectively.

Nucleus-independent chemical shifts (NICS), introduced in 1996, provide a simple and efficient magnetic criterion of aromaticity.^[15] NICS is based on the negative absolute magnetic shielding computed at the cluster centers or above the centers of

Table 2. Lifetimes and second order methanol quenching				
rate constants for 9-fluorenyl cation (1) and the thiophene				
fluorenyl cation analogs 2, 3, and 4 in deoxygenated HFIP				
solution at 25 °C.				

Cation	Lifetime (µs)	$k_{\rm MeOH} {\rm M}^{-2} {\rm s}^{-1}$
9-Fluorenyl cation (1) 2 3 4	10 19 15 8	$\begin{array}{c} (7\pm1)\times10^7 \\ (4.0\pm0.2)\times10^5 \\ (4.6\pm0.2)\times10^5 \\ (3.4\pm0.4)\times10^5 \end{array}$

the rings and clusters. NICS are now widely employed to characterize the aromaticity and antiaromaticity of two- as well as three-dimensional species and transition states.^[16–20] Negative NICS values (given in ppm) imply aromaticity (diatropic ring currents), and positive NICS values correspond to antiaromaticity (paratropic ring currents). In contrast to other aromaticity criteria, NICS does not require reference molecules, increment schemes, or equations for evaluation.^[15] Thus the degree of antiaromaticity of the four cations can also be assessed from the NICS data (Table 3) which suggest that cations **2** and **4** are more antiaromatic than fluorenyl (1) from the perspective of the middle ring, whereas ion **3** exhibits less antiaromatic character compared to **1**.

DISCUSSION

As expected based on the extensive studies that have been reported on the photochemistry of 9-fluorenol under various conditions,^[4,5,12,21] direct irradiation of the thiophene fluorenol analogs 5, 6, and 7 in pure MeOH solution involves both heterolysis and homolysis of the C-OH bond, to produce photoproducts derived from the corresponding carbocation (i.e. the methyl ethers 16, 18, and 20) and radical intermediates (i.e. hydrocarbons 10, 13, and 19 and ketones 15, 17, and 21), respectively. The ketones are produced from aerobic oxidation of the corresponding fluorenyl radicals by way of their hydroperoxide intermediates. The parent 9-fluorenyl hydroperoxide is known to undergo decomposition to fluorenone and fluorenol with elimination of molecular oxygen.^[22] It was found that purging the solutions with argon prior to irradiation suppressed the production of ketones 15, 17, and 21 with concomitant yield increase of the reduced products 10, 13, and 19. The yields of the methyl ethers derived from 5 and 6 are higher than that from 7, which appears to produce mainly radical-derived photoproducts. However, care must be exercised in the interpretation of the product yields reported in Table 1, as the methyl ethers can undergo secondary photolysis to yield the same radical-derived products as the alcohols,^[12] and no attempt was made to determine the true primary photoproduct yields in either MeOH or MeOH/HFIP mixtures. The distribution of homolysis and



Scheme 5. Computed relative energies for thiophene cations 2, 3, 4, and fluorenyl cation 1.

heterolysis products from photolysis of 9-fluorenol is known to depend critically on solvent polarity and acidity, with the relative yield of the cation increasing with increasing ionizing ability and acidity,^[21] cation **1** is formed essentially exclusively on photolysis of 9-fluorenol in the strongly acidic, non-nucleophilic solvent HFIP.^[12,21] Thus, the fact that the methyl ethers **16 18**, and **20** are observed in the photolyses of **4–6** in MeOH, even after extended irradiation, provides reasonably strong support for the expectation that the corresponding cations (**2–4**) should be the major primary products upon photolysis of the compounds in HFIP. Indeed, like 9-fluorenol itself,^[12] the yield of the methanolysis product **18** increased from 30 to 48%, at the expense of the radical-derived products **19** and **15**, upon irradiation of **6** in 3:1 MeOH-H₂O under similar conditions to those employed for the irradiations in pure MeOH.

This was also found to be the case for the ethers **16**, **18**, and **20** which underwent secondary photodecomposition to radical derived products. The relatively low yield of **20** from irradiation of alcohol **7** in methanol was enhanced using shorter irradiation

Table 3. Calculated NICS 1 A° above the five- and sixmembered ring centers (denoted as NICS (1) ppm) for following compounds at B3LYP/6-311 + G^{**} levels

	NICS(0) _{total} /NICS(1) _{total}			
Cation	6MR	5MR	5MR(S)	
1	+10.1/4.90	+27.0/18.4		
2	+10.10/5.37	+30.22/21.44	+3.27/2.85	
3	+4.07/0.10	+17.79/10.99	+2.80/4.39	
4	+13.45/+8.27	+36.47/+26.33	+3.63/+4.3	

times (irradiation for 30 min gave 11% of **20** (*vida supra* Table 2)) or by the addition of HFIP (20% of **20** in a 25% v/v of HFIP/ methanol for 15 min UV exposure time). However, the limited solubility of alcohol **7** in HFIP, as well as the lack of an authentic HFIP solvolysis product precluded preparative photoproduct studies in this solvent. Such solvent dependent behavior on the relative extent of heterolytic and homolytic C—O bond scission in 9-fluorenol has been reported from differences in lifetimes and decay features measured for the corresponding cation and radical transients.^[21]

Our assignment of the promptly formed transients observed in the laser flash photolysis experiments with 5-7 to the corresponding carbocations rests mainly on the similarity of their absorption spectra to that of 1 and the fact that they are quenched by MeOH, albeit 20-30 times less rapidly than 1 under similar conditions. We were initially concerned that these reactions appear to proceed via overall third-order kinetics (first order in cation, second order in alcohol) in all four cases, because of the report by McClelland et al of a second-order rate constant for reaction of 1 with water in HFIP solution $(k_{H2O} \sim 1.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1})$.^[5] However, this value was derived from data recorded over the 0-0.5 M concentration range in added water, where the variation in the cation decay rate constant with [H₂O] was "approximately linear". In fact a plot of the reported k_{decav} values vs. [H₂O] for this system over the complete concentration range studied reveals an almost perfect squared dependence of the rate on concentration, similar to what we have found in the present work for guenching of 1-4 by MeOH; a plot of k_{decay} versus $[H_2O]^2$ yields a slope of $k_{H2O} = (9.41 \pm 0.07) \times 10^5 \text{ M}^{-2} \text{ s}^{-1}$. This is roughly 20 times lower than the value measured here for MeOH quenching under similar conditions, and is line with the known relative reactivities of water and methanol solvents toward carbocations.^[5,23,24]

While McClelland *et al* suggested that the non-linear quenching behavior might be due to solvation effects,^[5] we

$$Ar_{2}C^{+}-H + MeOH \xrightarrow{K_{1}} \begin{bmatrix} + & H \\ MeO^{+} & H \\ Ar_{2}C^{-}-H \end{bmatrix} \xrightarrow{k_{2}[MeOH]} OMe \\ Ar_{2}C^{-}-H + MeOH_{2}^{+}$$

Scheme 6. Mechanism for methanol quenching of cations 2-4.

suggest that a more reasonable explanation is provided by the mechanism of Scheme 6, in which initial nucleophilic attack is followed by general base catalyzed deprotonation of the first-formed intermediate,^[25–27] with a second molecule of alcohol acting as the general base.

Computed charge densities for 9-fluorenyl cation 1 shows a +0.145 positive charge at C-9 with the remaining charge delocalized about the other atoms. However, for ions 2–4 significant positive charge resides on sulfur (+0.59 for 2, +0.54 for 3, and +0.63 for 4) with much less charge on the nucleofugal carbon. This is broadly consistent with the observation that cations 2–4 are all 20–30 times less reactive toward MeOH than the parent cation, 1; the decrease in positive charge density at the nucleofugal carbon results in an increase in the kinetic barrier for nucleophilic attack. It should be noted that while the differences in positive charge density at sulfur in 2–4 are relatively small, they appear to correlate (inversely) with the rate constants for reaction of the three cations with MeOH, with the smallest rate constant being obtained for cation 4, in which positive charge density at sulfur is highest (and that on the nucleofugal carbon is lowest).

The antiaromatic character of the fluorenyl cation has been convincingly established by theoretical and experimental studies.^[28,29] The recent theoretical studies by Herndon and Mills^[28] indicate an average destabilization energy for cation 1 of 16.3 ± 1.6 kcal/mol with specific values dependent on the reference system which corrects for strain, non-aromatic stabilization and other structural effects.^[28] Our value of 9.7 kcal/mol for the destabilization energy of cation 1 falls somewhat lower due to the different reference system chosen in our study for comparison with the corresponding benzhydryl analogs which is the common standard for computing aromatic stabilization energies of fluorenyl ions. While it may be argued that the differences of computed relative stabilization energies for ions 2, 3, and 4 fall within the deviation of $1.6 \text{ kcal/mol}^{[28]}$ depending on the choice of the reference system and thus not significant, the independent NICS values determined for these ions corroborate the trend for the destabilization energies.

SUMMARY AND CONCLUSIONS

Precursor alcohols for the photogeneration of the three regioisomeric thiophene cation equivalents of 9-fluorenylcation were prepared. These alcohols on photoexcitaion generated the corresponding cations which were quenched in methanol as evident from the formation of the methanolysis products. In addition, products derived from the corresponding radicals were evident from the presence of reduced (indenothiophenes) as well as oxidized (indenothiophenones) materials in the photomixture which distribution was dependent on irradiation times and solvent composition. Time resolved photoexcitation permitted the direct observation of the three regioisomeric cations which were quenched by methanol following second order kinetics. The relative thermodynamic stabilities of the fluorenyl cation analogs were assessed using MO calculations for the isodesmic reactions

of hydride transfer to the open form cation equivalents. Based on this scheme, cations 2 and 4 are less stable than 9-fluorenyl cation (1), whereas 3 is more stable than 1. These data are corroborated by the calculations of the NICS values for the middle ring which show that 2 and 4 are more antiaromatic than 9-fluorenyl cation whereas 3 is less antiaromatic than 1. The kinetic reactivity of the three regioisomeric cations are roughly two orders of magnitude less than 9-fluorenyl cation, and is likely associated with the lower positive charge density of the nucleofugal carbon as a result of charge delocalization to the sulfur.

EXPERIMENTAL

All reactions were done in dried glassware. All solvents used for the reactions were dried and distilled. THF and diethyl ether were dried using sodium metal. 1,1,1,3,3,3-Hexafluoro-2-propanol (Sigma–Aldrich) was purified by distillation over sodium borohydride. Proton NMR spectra were obtained on a Bruker ARX-400 spectrometer and ¹³C NMR was carried out on a Bruker 300 spectrometer. Solutions in 99.8% CDCl₃ with 1% TMS as an internal standard were used. Methanol-d₄ and DMSO-d₆ were used for certain samples for solubility reasons, and are noted where appropriate. Photolyses were carried out using a Hanovia 450W medium pressure mercury arc lamp. Melting points were determined on a Reichert melting point apparatus and are uncorrected. Mass Spectra were collected (El mode) using a Varian Series 4000 GC/MS/MS spectrometer.

Methyl 2-(3-thienyl)benzoate (8)¹¹

In a 250 mL round-bottom flask with a magnetic stirrer, was added methyl 2-iodobenzoate (5.3 mL) benzene (120 mL). 2 M Sodium carbonate (36 mL) was added to the benzene solution. 3-Thiophene boronic acid (3.07 g) dissolved in ethanol (22 mL) was added to this solution. The mixture was purged with argon. After 30 min, 270 mg of tetrakis(triphenylphosphine)palladium(0) was introduced. Under argon atmosphere, the mixture was stirred and refluxed overnight. The flask and condenser were wrapped in aluminum foil to protect the reaction from light. After the reaction was complete, the mixture was poured into a separatory funnel. The organic layer was extracted with dichloromethane (100 mL) and washed with saturated sodium chloride solution (50 mL) then washed with water (3×100 mL). Methyl 2-(3-thienyl)benzoate was purified by column chromatography (ethyl acetate:hexane 5:95 by volume). An oily material was obtained (5.54 g, quantitative). ¹**H NMR** δ : 7.82 (d, J = 7.0 Hz, 1H), 7.52 (m, 1H), 7.4 (m, 4H), 7.28 (m, 1H), 3.75 (s, 3H). These data are inconsistent with those reported.^[30] The literature describes this compound as a solid (m.p. 151-152 °C) and showing a molecular ion mass of m/z = 192 which is inconsistent with the molecular mass for this compound. The correct assignment for the structure of this ester was confirmed by hydride reduction to the known alcohol 9 (see below).

[2-(3-Thienyl)phenyl]methanol (9)

Methyl 2-(3-thienyl)benzoate (5.54 g) was dissolved in dry THF (150 mL). Lithium aluminum hydride (1.0 g) was added and the solution was left to stir for 1 h. Water (10 mL) was then added to quench the reaction. The THF was partially evaporated and the product was acidified with 1 M HCl (2 mL), extracted with dichloromethane (100 mL) and washed with water (100 mL). Yield 2.03 g of oily material (42%) which was used for the next step without further purification. ¹H NMR δ : 7 · 57 (d, 1 H, *J* = 7.1 Hz), 7.48 (d, 1 H, *J* = 7.0 Hz), 7.43–7.34 (m, 3 H), 7.20 (d, 1 H, *J* = 3.0 Hz), 7.13 (t, 1 H), 4.78 (s, 2 H), 1.80 (s, br, 1 H); ¹³C NMR δ 141.5, 138.6, 133.7, 130.9, 128.9, 128.3, 127.9, 127.5, 127.0, 125.8, 63.5, 4.7 (s, 2H), 1.8 (s, 1H, OH). These spectra were identical with those for an authentic sample obtained commercially.

8H-Indeno[2,1-b]thiophene (10)

PPA (50 mL) was heated to 120 °C with stirring. [2-(3-Thienyl) phenyl]methanol (2.03 g) was added along with some dichloromethane for quantitative transfer and heated for 2 min. This mixture was then poured into ice water (300 mL) and extracted with dichloromethane (3 × 100 mL). The product was purified by column chromatography twice (ethyl acetate:hexane 5:95 by volume) yielding 1.27 g (69%) of a white solid m.p. 65–67 °C (lit.^[31] m.p. 66–67 °C). ¹H NMR δ : 7.57 (d, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 7.4 Hz, 1H), 7.35 (m, 3H), 7.21 (t, *J* = 7.4 Hz, 1H), 3.85 (s, 2H).

8H-Indeno[2,1-b]thiophen-8-ol (5)

8H-Indeno[2,1-b]thiophene (10) (1.27 g) was dissolved is carbon tetrachloride (200 mL). One molar equivalent of NBS (1.31 g) was added and the solution left to stir and reflux with a 100 W lamp directed on the solution for 3 h. The solution was filtered and washed with water (100 mL) in a separatory funnel, and then the solvent was evaporated under vacuum. The crude 8-bromo-8H-indeno[2,1-b]thiophene was dissolved in a 50:50 solution of acetone and water (200 mL) containing a 1 mol eq. of silver nitrate (1.25 g) and allowed to stir for 15 min. After the reaction was complete the solution was filtered and extracted with diethyl ether (100 mL) and washed with water (2×100 mL). The organic extract was dried over anhydrous magnesium sulfate. The crude product was purified by column chromatography (ethyl acetate:hexane 5:95 by volume) and yielded 604.5 mg of 8H-indeno[2,1-b]thiophene-8-ol in 44% yield. **m.p.**: 115–117 °C (lit.^[32] m.p. 116 °C). IR: $\nu = 3292$, 3194, 1026 cm⁻¹; ¹H NMR δ : 7.56 (d, J = 7.4 Hz, 1H,), 7.44 (d, J = 4.8 Hz,1H), 7.41 (d, J = 7.35 Hz, 1H), 7.33 (t, J = 7.35 Hz, 1H), 7.24 (t, J = 7.4 Hz, 1H), 7.23 (d, J = 4.9 Hz, 1H), 5.4 (br s, 1H), 2.3 (br s, 1H, OH). ^{13}C NMR $\delta:$ 149.5, 146.82, 146.75, 137.5, 131.0, 128.9, 125.8, 124.8, 119.3, 118.7, 72.7; MS: m/z (% intensity): 188 (M ⁺,100), 171 (42), 115 (41).

Methyl 2-(2-thienyl)benzoate (11)¹¹

In a 250 mL round-bottom flask with a magnetic stirrer, methyl 2-iodobenzoate (3.44 mL) was added to benzene (80 mL). To this solution was added 2 M sodium carbonate (24 mL), and 2-thiophene boronic acid (2.0 g) dissolved in ethanol (15 mL). The mixture was purged with argon. After 20 min, 180 mg of tetrakis(triphenylphosphine)palladium(0) was introduced into the mixture. Under argon atmosphere, the mixture was stirred and refluxed overnight. After the reaction was complete, the

mixture was poured into a separatory funnel. The organic layer was extracted with diethyl ether (150 mL) and washed with saturated sodium chloride solution (50 mL) then washed with water (3 × 100 mL). Methyl 2-(2-thienyl)benzoate was purified by column chromatography (ethyl acetate:hexane 5:95 by volume). An oily product (2.24 g, 66%) was obtained. ¹H NMR δ : 7.7 (d, J = 7.5 Hz, 1H), 7.45 (m, 2H), 7.3 (m, 2H), 7.0 (m, 2H), 3.7 (s, 3H). The NMR data are consistent with those reported in the literature.^[33]

[2-(2-Thienyl)phenyl]methanol (12)

Methyl 2-(2-thienyl)benzoate (2.24 g) was dissolved in THF (50 mL). A molar equivalent of lithium aluminum hydride (390 mg) was added and the solution was left to stir for 40 min at room temperature. Another equivalent of lithium aluminum hydride (390 mg) was added and the solution was left to stir for another 30 min. Water (10 mL) was then added to quench the reaction. The solvent was partially evaporated and the product was extracted with diethyl ether (100 mL) and washed with water (100 mL). 1.47 g of [2-(2-thienyl)phenyl]methanol was obtained in 75% yield. M.p. $60-62 \degree C$. ¹H NMR δ : 7 · 54 (m, 1 H), 7.3–7.5 (m, 5 H), 7.20 (d, 1 H, J = 3.0 Hz), 7.24 (m, 1 H), 4.69 (d, 2 H, J = 3.7 Hz), 1.81 (s, br, 1 H).; ¹³C NMR: δ : 140.8, 138.1, 136.2, 130.1, 128.9, 127.9, 127.7, 125.5, 123.2, 63.5. This sample was identical in all respects with an authentic commercial sample.

4H-Indeno[1,2-b]thiophene (13)

PPA (20 mL) was heated to 120 °C with stirring. [2-(2-Thienyl)phenyl]methanol (1.47 g) was added with some dichloromethane for quantitative transfer and heated for 4 min. This mixture was then poured into ice water (50 mL) and extracted with dichloromethane (3 × 100 mL). The product was purified by column chromatography (ethyl acetate:hexane 5:95 by volume). 4H-Indeno[1,2-b]thiophene (**13**) was obtained (229.4 mg, 17%) as a white solid, m.p. 67–68 °C (lit.^[34] m.p. 68–69 °C). ¹H NMR δ : 7.52 (dxd, *J* = 7.4 Hz, 7.6 Hz, 2H), 7.35 (m, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 4.7 Hz, 1H), 3.75 (s, 1H).

4H-Indeno[1,2-b]thiophen-4-ol (7) via

4-bromo-4H-indeno[1,2-b]thiophene

4H-Indeno[1,2-b]thiophene (229.4 mg) was dissolved is carbon tetrachloride (125 mL). One molar equivalent of NBS (237 mg) was added and the solution was left to stir and reflux with a 100 W lamp directed on the solution for 2.5 h. Following this the solution was filtered and washed with water (100 mL) in a separatory funnel, and then the solvent was evaporated under vacuum. The crude 4-bromo-4H-indeno[1,2-b]thiophene was dissolved in a 50:50 solution of acetone and water (160 mL) containing a molar equivalent of silver nitrate (225 mg) and allowed to stir for 10 min. After the reaction was complete the solution was filtered and extracted with diethyl ether (100 mL), washing with water (2×100 mL). The extract was dried with anhydrous magnesium sulfate. The crude product was purified by column chromatography (ethyl acetate:hexane 20:80 by volume) and yielded 50 mg of 4H-indeno[1,2-b]thiophen-4-ol as well as 52 mg of 4H-indeno[1,2-b]thiophen-4-one (21). For 4H-indeno[1,2-b]thiophen-4-ol: **m.p**.: 148–150 °C. IR: $\nu = 3369$, 3304, 1053 cm⁻¹; ¹**H** NMR δ : 7.53 (d, J = 8.4 Hz, 1H), 7.3 (m, 3H), 7.2 m 1H), 7.18 (d, J = 4.8 Hz, 1H), 5.4 (s, 1H), 3.85 (s, 1H, OH). ¹³C NMR δ: 150.3, 148.7, 143.9, 136.9, 129.0, 128.2, 126.2, 124.9, 122.7, 119.0, 72.3. MS: m/z: 188 (100), 171 (26), 115 (60); Anal. Calc. for C₁₁H₈OS: C, 70.21; H, 4.26. Found: C, 69.89; H, 3.88.

4H-Indeno[1,2-b]thiophen-4-ol (7) via

4H-indeno[1,2-b]thiophen-4-one (21)

The remaining 4H-indeno[1,2-b]thiophen-4-one (52 mg) from the previous step was dissolved in methanol (100 mL) and three equivalents of sodium borohydride (30 mg) were added and allowed to stir for 1.5 h. The solution was then guenched with water and the methanol partially evaporated. This mixture was extracted with diethyl ether (100 mL) and washed with water (100 mL) in a separatory funnel. The purified product was obtained by column chromatography (ethyl acetate:hexane 20:80 by volume) yielding 47.5 mg of 4H-indeno[1,2-b]thiophene-4-ol and when combined with the previous 4H-indeno[1,2-b]thiophene-4-ol resulted in a total yield of 97.5 mg (39% yield).

3-Bromo-4-phenylthiophene¹¹

To a benzene solution (120 mL) of 3,4-dibromothiophene (4.44 g) was added 2 M aqueous sodium carbonate solution (37.5 mL). Phenyl boronic acid (2.25 g), dissolved in ethanol (22.5 mL) was added. The mixture was purged with argon. After 20 min, 225 mg of tetrakis(triphenylphosphine)palladium(0) was introduced into the mixture. The mixture was stirred and refluxed under argon overnight. The flask and condenser were wrapped in aluminum foil to protect the reaction from light. After the reaction was complete, it was extracted with dichloromethane (100 mL) and washed with saturated sodium chloride solution (50 mL) then with water (3 \times 100 mL). The product was purified by column chromatography (hexane), (2.98 g, 68% yield). m.p.: 63–67 °C (lit.^[34] m.p. 69–70 °C) ¹H NMR δ: 7.47 (m, 2H), 7.35 (m, 4H), 7.2 (m, 1H).

4-Phenylthiophene-3-carboxylic acid (14)

Under an argon atmosphere, n-butyl lithium (5 mL, 2.5 M in hexanes) was added to a solution of 3-bromo-4-phenylthiophene (2.98 g) dissolved in dried diethyl ether (60 mL) and was slowly added over a period of 10 min at -78 °C. This reaction mixture was left to stir for 20 min. Dry carbon dioxide was bubbled into the reaction mixture for 1 h. Water (10 mL) was then added to quench the reaction and the solution was washed with diethyl ether (100 mL) in a separatory funnel. The aqueous phase was then acidified with 1 M HCl (2 mL) and extracted with diethyl ether (100 mL). Yield 2.21g (87% yield). m.p.: 195-197 °C (lit.^[34] m.p. 206–208 °C). ¹H NMR δ: 8.31 (m, 1H), 7.4(m, 5H), 7.21(m, 1H), 5.2(s, 1H, COOH).

8H-Indeno[1,2-c]thiophen-8-one (15)

PPA (15 mL) was heated to 200 °C in a large test tube using a Bunsen burner. 4-Phenylthiophene-3-carboxylic acid (1 g) was added to the PPA and heated for 2-3 min. The hot mixture was poured into ice water (50 mL) and extracted with dichloromethane (3 \times 75 mL). The same procedure was repeated on the remaining 1.11 g of starting material. The product was separated and purified by column chromatography (ethyl acetate:hexane 20:80). A white solid was obtained (237 mg, 12%), m.p. 90–93 $^{\circ}$ C (lit.^[34] m.p. 92–93 °C). ¹H NMR δ: 7.76 (d, 1H, *J* = 1.71 Hz), 7.67 (d, 1H, J = 7.48 Hz), 7.5 (m, 2H), 7.28 (m, 1H), 7.14(m, 1H).

8H-Indeno[1,2-c]thiophene-8-ol (6)

8-H-Indeno[1,2-c]thiophene-8-one (237 mg) was dissolved in methanol (50 mL). To this solution was added sodium borohydride (50 mg) and the solution allowed to stir for 10 min. The reaction mixture was then quenched with water (10 mL) and the methanol partially evaporated. The product was extracted with diethyl ether (100 mL) and washed with water (100 mL). Yield 230 mg. (96%) m.p.: 135–137 °C. IR: ν = 3302, 3202, 1026 cm⁻¹; ¹H **NMR** δ: 7.58 (d, 1H, J = 7.5 Hz), 7.51 (d, 1H, J = 7.2 Hz), 7.3 (m, 3H), 7.2 (d, 1H, J = 2.2 Hz), 5.5 (d, 1H, J = 8.5 Hz), 2.2 (d, 1H, J = 9.1 Hz). ¹³C NMR δ: 150.5, 149.1, 145.2, 136.1, 129.0, 127.5, 126.0, 120.7, 119.6, 112.9, 70.4.MS: m/z: 188 (M⁺, 100), 171 (17), 115 (40). Anal. Calc. for C₁₁H₈OS: C, 70.21; H, 4.26. Found: C, 70.02; H, 3.98.

Photolysis in methanol

Approximately 40 mg of each isomer: 8H-indeno[2,1-b]thiophene-8-ol, 8H-indeno[1,2-c]thiophen-8-ol and 4H-indeno[1,2-b] thiophen-4-ol was dissolved in methanol (25 mL) and placed in separate quartz tubes. These solutions were purged with argon for approximately 10 min. The tubes were then attached to a cooling immersion well containing a Hanovia 450W medium-pressure mercury arc lamp and irradiated for 1 h. The irradiated solutions were evaporated in vacuo and the residue was separated by preparative TLC (10:90 ethyl acetate:hexane). ¹H NMR spectra were acquired for each fraction and compared with reference samples prepared above.

Preparation of methyl ethers 16, 18 and 20

8-Methoxy-8H-Indeno[2,1-b]thiophene (16)

8H-Indeno[2,1-b]thiophene (10) (45 mg) was dissolved in carbon tetrachloride (5 ml). NBS (52 mg) was added and the mixture left to stir and reflux with a 100 W lamp directed on the mixture for 90 min. After cooling, the reaction mixture was filtered and washed with hexane, and then the solvents were removed by evaporation under vacuum. The residue was dissolved in a small amount of acetone, followed by addition of methanol (20 ml) and AgNO₃ (49 mg). The resulting suspension was stirred for 30 min at room temperature. After filtering, the filtrate was evaporated under vacuum, and the crude product was purified on silica column using gradient elution of 0-10% ether in hexanes, resulting in 30 mg of **16** as a gummy residue (56%). ¹**H NMR** δ 7.54 (d, 1H, J = 7.3 Hz), 7.42–7.47 (m, 2H), 7.36 (t, 1H, J = 7.3 Hz), 7.20-7.27 (m, 2H), 5.54 (s, 1H), 3.28 (s, 3H), ¹³C-NMR δ 148.1, 146.5, 143.3, 138.4, 131.2, 128.9, 125.6, 125.2, 119.3, 118.7, 79.4, 53.5; MS (GC/MS): m/z 202.1 (M⁺, 74), 187 (100), 171 (80), 115 (40). Anal. **Calc**. for C₁₂H₁₀OS: C, 71.29; H, 4.95. Found: C, 71.10; H, 5.12.

8-Methoxy-8H-indeno[1,2-c]thiophene (18)

8-H-Indeno[1,2-c]thiophen-8-ol (6) (24 mg) was treated with two drops of SOCl₂ in CDCl₃ (1 ml) and left to stir for 0.5 h at room temperature. After removing solvents by rotary evaporation under reduced pressure, methanol (10 ml) was added to dissolve the residue, and then a solution of AgNO₃ (27 mg) in methanol was added. The resulting suspension was stirred for 15 min at room temperature. After filtering, the filtrate was evaporated under reduced pressure, and the crude was purified on silica column using gradient elution of 0-10% ether in hexanes, resulting in 22 mg of **18** as a gummy residue (85%). ¹**H-NMR** δ 7.56 (t, 1 H), 7.38 (t, 1 H), 7.34-7.28 (m, 2 H), 7.24 (d, 1 H, J = 1.8 Hz),

5.51 (s, 1 H), 3.28 (s, 3 H).; ¹³C-NMR δ 147.7, 146.2, 145.9, 137.1, 129.1, 127.3, 126.5, 120.7, 119.8, 112.7, 77.1, 53.6; MS (GC/MS) *m/z* 202.1 (M⁺, 79), 187 (60) 171 (80), 115 (35). **Anal. Calc.** for C₁₂H₁₀OS: C, 71.29; H, 4.95. Found: C, 71.51; H, 4.72.

4-Methoxy-4H-Indeno[1,2-b]thiophene (20)

This isomer was prepared by using the same procedure as that for **16** except that 4H-indeno[1,2-b]thiophene (**13**) was used as the starting material. ¹H NMR δ 7.54 (d, 1H, *J* = 7.4 Hz), 7.26–7.19 (m, 2H), 5.42 (s, 1H), 3.22 (s, 3H); ¹³C-NMR δ 147.4, 145.7, 144.8, 137.7, 129.0, 127.8, 125.9, 125.2, 123.1, 119.0, 78.7, 53.3; **MS** (GC/MS) *m/z* 202.1 (M⁺, 91), 187 (95), 171 (100), 115 (38). **HRMS** calc. for C₁₂H₁₀OS (M) 202.0452, found 202.0454.

Laser flash photolysis

Nanosecond laser flash photolysis experiments employed the pulses (248 nm; ca. 20 ns; ca. 100 mJ) from a Lambda-Physik Compex 120 excimer laser filled with F₂/Kr/He mixtures, and a Luzchem Research mLFP-111 laser flash photolysis system, modified as described previously.^[35] Solutions were prepared at concentrations such that the absorbance at the excitation wavelength was between ca. 0.7 and 0.9. For transient spectra, solutions were flowed continuously through a thermostatted $7 \times 7 \,\text{mm}$ Suprasil flow cell connected to a calibrated 100 mL reservoir, fitted with a glass frit to allow bubbling of argon gas through the solution. A Masterflex[™] 77390 peristaltic pump fitted with Teflon tubing (Cole-Parmer Instrument Co.) was used to pump the solution from the reservoir through the sample cell at controlled rates. Solution temperatures were measured with a Tefloncoated copper/constantan thermocouple inserted into the thermostated sample compartment in close proximity to the sample cell.

Quenching experiments were carried out in 7×7 mm Suprasil cells, which were replaced regularly throughout each experiment with fresh solution in order to maintain adequate transient signals. Appropriate amounts of MeOH were added by microlitre syringe, as the neat liquid in the cases of 2-4 or as a standard solution in HFIP in the case of 2-fluorenol. Transient decay constants were calculated from traces recorded at or near the absorption maxima using the manufacturer's software, or by non-linear least squares analysis of the absorbance-time profiles using the Prism 5.0 software package (GraphPad Software, Inc.) and the appropriate user-defined fitting equations, after importing the raw data from the Luzchem mLFP software. Rate constants were calculated by linear or non-linear least-squares analysis of decay rate-concentration data (at least 7 points) that spanned as large a range in transient decay rate as practically possible. Errors are quoted as twice the standard deviation obtained from the least-squares analyses.

Theoretical Calculations

Calculations were carried out at the B3LYP/6-311 + G^{**} //B3LYP/ 6-311 + G^{**} level using GAUSSIAN 2003.^[36] The energies were corrected using calculated zero-point vibrational energies.

REFERENCES

- [1] R. Breslow, Chem. Eng. News 1965, June 28, 90-99.
- [2] R. Breslow, Acc. Chem. Res. 1973, 6, 393-398.

- [3] A. Allen, T. T. Tidwell, Chem. Rev. 2001, 101, 1333-1348.
- [4] S. L. Mecklenburg, E. F. Hilinski, J. Am. Chem. Soc. 1989, 111, 5471–5472.
- [5] R. A. McClelland, N. Mathivanan, S. Steenken, J. Am. Chem. Soc. 1990, 112, 4857–4861.
- [6] T. Amyes, M. Richard, M. Novak, J. Am. Chem. Soc. 1992, 114, 8032–8041.
- [7] H. Jia, Pv. R. Schleyer, Y. Mo, M. A. McAllister, T. T. Tidwell, J. Am. Chem. Soc. 1997, 119, 7075–7083.
- [8] C. F. Rodriquez, D. L. Vukovic, A. C. Hopkinson, J. Mol. Struct. (THEOCHEM) 1996, 363, 131–138.
- [9] A. R. Katritzky, M. Karelson, S. Sild, T. M. Krygowski, K. Jug, J. Org. Chem. 1998, 63, 5228–5231.
- [10] S. G. Lias, J. F. Liebman, R. D. Levin, J. Phys. Chem. Ref. Data 1984, 13, 695–808.
- [11] Hark. Richard, R Hauze. Diane, B Petrovskaia. Olga, Joullie. Madeleine, M Tetrahedron Lett. 1994, 35(42), 7719–7722.
- [12] P. Wan, E. Krogh, J. Am. Chem. Soc. 1989, 111, 4887-4895.
- [13] R. A. McClelland, F. L. Cozens, J. Li, S. Steenken, J. Chem. Soc., Perkin Trans. 2: Phys. Org. Chem. 1996, 1531–1543.
- [14] F. Cozens, J. Li, R. A. McClelland, S. Steenken, Angew. Chem. 1992, 104, 753–755 (See also Angew. Chem., Int. Ed. Engl., 1992, 31, 743-5).
- [15] Pv. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. Rv. E. Hommes, J. Am. Chem. Soc. 1996, 118, 6317.
- [16] S. Patchkovskii, W. Thiel, J. Mol. Model. 2000, 6, 67 and references cited
- [17] D. Sawicka, S. Wilsey, K. N. Houk, J. Am. Chem. Soc. 1999, 121, 864
- [18] M. Buhl, Chem. Eur. J. 1998, 4, 734.
- [19] A. R. Lera, R. Alvarez, B. Lecea, A. Torrado, F. P. Cossio, Angew. Chem., Int. Ed. 2001, 40, 557
- [20] S. P. Verevkin, H.-D. Beckhaus, C. Ruckhardt, R. Haag, S. I. Kozhushkov, T. Zywietz, A. deMeijere, H. Jiao, P. v. R. Schleyer, J. Am. Chem. Soc. 1998, 120, 11130.
- [21] G. G. Gurzadyan, S. Steenken, Chem. Eur. J. 2001, 7, 1808–1815.
- [22] L. Zhang, G. D. Mendenhall, J. Photochem. Photobiol. A: Chem. 1997, 107, 169.
- [23] J. P. Richard, M. E. Rothenburg, W. Jencks, J. Am. Chem. Soc. 1984, 106, 1361.
- [24] R. A. McClelland, V. M. Kanagasabapathy, N. Banait, S. Steenken, J. Am. Chem. Soc. 1988, 110, 6913.
- [25] F. L. Cozens, N. Mathivanan, R. A. McClelland, S. Steenken, J. Chem. Soc. Perkin Trans. 2, 1992, 2083.
- [26] J. R. Gandler, J. Am. Chem. Soc. 1985, 107, 8218.
- [27] R. Ta-Shma, W. P. Jencks, J. Am. Chem. Soc. 1986, 108, 8040.
- [28] W. C. Herndon, N. S. Mills, J. Org. Chem. 2005, 70, 8492-88496.
- [29] S. Pogodin, I. Agranat, J. Org. Chem. 2007, 72, 10096–10107.
- [30] N. M. Chaignon, I. J. S. Fairlamb, A. R. Kapdi, R. J. K. Taylor, A. C. Whitwood, J. Mol. Catal. A 2004, 219, 191–1199.
- [31] D. W. H. MacDowell, T. B. Patrick, J. Org. Chem. 1967, 32, 2441–2445.
- [32] C. L. Arcus, G. C. Barrett, J. Chem. Soc. 1960, 2098–2102.
- [33] F. Sieber, P. Wentworth, K. Janda, J. Comb. Chem. **1999**, 1, 540–546.
- [34] D. W. H. MacDowell, A. T. Jeffries, J. Org. Chem. **1970**, 35, 2441–2445.
- [35] W. J. Leigh, C. R. Harrington, I. Vargas-Baca, J. Am. Chem. Soc. 2004, 126, 16105.
- [36] Gaussian 2003: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. M. Millam, S. S. Lyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al_Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, Revision B.05; Gaussian, Inc.: Pittsburgh, PA, (2003).