truly localized at the CTL/air interface resulting in a negligible light-induced fatigue. Electrical conduction through the photoconductor is thus not effected by exposure to the shorter wavelength light, but a very thin film of CTL has its DEH converted to IND. Concomitantly, the electrical conductivity parallel to the surface is effected because IND has a higher oxidation potential; this is an important observation because it directly effects resolution, or in other words the ability to produce hard copies with very small images.

### Concluding Remarks and Summary

Electrophotographic processes, used in copiers and printers, place stringent demands on organic photoconductors. Although a photoconductor is subjected to several charge and discharge steps to produce one copy, the cycle is repeated about $10^3$–$10^6$ during the normal lifetime of the photoconductor. For the electrophotographic process to operate successfully, the electrical properties, that is, resistivity, conductivity, dark and light voltage, and dark and light decay, must remain as constant as possible. When this is not the case, the photoconductor is said to suffer "fatigue" and one searches to explain its cause and as a result offer a fix. This task is not at all trivial because one seeks to relate how the flow of very small photocurrents are effected by small physical and/or chemical changes in the organic materials. We present here a model photoconductor with which we have studied the effect of photochemistry using "blue light" on the hole-transporting material, DEH, in the charge-transport layer. A clear and direct relation is found between DEH photochemistry and an increase in residual voltage. To add another layer of validity in support of our conclusions, we synthesized a new DEH derivative that is identical with DEH in every property but has its photochemical activity toward blue light reduced by about 2–3 orders of magnitude. Replacing DEH with this material in the photoconductor in effect eliminates the blue light fatigue and hence firmly establishes a relation between photochemistry and electrical properties.

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# Design, Synthesis, Characterization, and Use of All-Organic Nonionic Photogenerators of Acid

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A study was made of the effects on thermal stability of varying the substitution patterns on 2-nitrobenzyl benzenesulfonate photogenerators of acid. It was found that the thermal stability of these sulfonate esters was dramatically increased by the introduction of an electron withdrawing, sterically bulky group (Br, $CF_3$) at the ortho position of the benzyl moiety. This enhancement in thermal stability allowed synthetic access to thermally stable photogenerators of acid based on powerful acids such as 2,2,2-trifluoroethanesulfonic acid.

## Introduction

In recent years the drive toward smaller feature sizes in the microelectronics industry has led to the development of chemically amplified photoresists. These resists possess an inherently high sensitivity because upon irradiation an initial photonic event generates a catalyst that can then promote a cascade of chemical reactions that completely transforms the irradiated portion of the resist.[1] One type on chemically amplified photoresist depends of the photogeneration of a protic acid.[2,3]

Until recently, photogeneration of such acids for use in chemically amplified resists required the use of onium salt materials such as triphenylsulfonium hexafluoroarsenate[2,3] which contained metal atoms. More recently, nonmetallic versions of these onium salts such as diphenyliodonium triflate have been described.[4] We have previously described the use of 2-nitrobenzyl sulfonate esters as covalent, highly soluble, nonmetallic photogenerators of tosic acid.[5-7] Other workers have reported covalent compounds capable of photogenerating nonactivated aryl sulfonic acids,[8-11] methanesulfonic acid,[12] and hydrogen halides.[13,14] However, these systems all release acids having relatively nucleophilic anions compared with hexafluoroarsenic and triflic acid, which can be formed by the irradiation of onium salts. This nucleophilicity may limit the catalytic chain lengths of the photogenerated acids and render such acid generators less effective in promoting certain chemical processes such as the catalytic deprotection of poly-

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([(*tert*-butyloxycarbonyl)oxy]-α-methylstyrene).[7] Although the onium salts can photogenerate strong acids, their photolysis involves as a key step the photogeneration of radicals and radical cations. These species may lead to undesirable competitive processes. For 2-nitrobenzyl sulfonate based photogenerators of acid, the acid is formed through the well-known *o*-nitrobenzyl rearrangement,[15] which is a photochemically induced intramolecular rearrangement in which no free radicals are produced in the main photochemical event. Moreover, since nitro compounds are well-known inhibitors[16] for radical processes, the effect of any radicals produced by secondary processes should be minimal. Therefore, it was of interest to synthesize 2-nitrobenzyl sulfonate esters of strong acids. To accomplish this, a detailed examination has been made of the effects of adding various substituents onto the 2-nitrobenzyl benzenesulfonate molecule at both the aryl ring of the 2-nitrobenzyl group and the aryl ring of the benzenesulfonate group. This was done to better understand the effects of steric and electronic substituent factors on the physical and chemical properties of the materials. This understanding in turn allowed ester structures to be designed that fulfill some of the application-specific requirements of a photogenerator of acid such as thermal stability, quantum yield, solubility, and catalytic chain length for *tert*-butoxycarbonyl (*t*-BOC) removal from (*tert*-butoxycarbonyl)oxy-functionalized polymers. In general, it was expected that structural modification would have the following effects: The inclusion of an electron-withdrawing substituent on the benzenesulfonate moiety would increase the acidity but decrease thermal stability, while substitution with such groups on the benzyl moiety would increase thermal stability. In particular, electron-withdrawing groups that do not absorb 248-nm radiation were examined to avoid possible interference with the photochemical deprotection of the 2-nitrobenzyl derivative. Selected 2-nitrobenzyl chromophores also allowed access to thermally stable esters based on the powerful acids 2,2,2-trifluoroethanesulfonic acid (tresic acid) and pentafluorobenzenesulfonic acid. The expectation was that these acids, which have counterion nucleophilicities intermediate between those of triflate and tosylate,[17] should have improved catalytic chain lengths over tosylate derivatives for *t*-BOC removal. The triphenylsulfonium and diphenyliodonium salts of tresic acid were also prepared for comparison. The base polymer chosen for these studies was poly([(*tert*-butyloxycarbonyl)oxy]styrene sulfone) (TBSS).

## Experimental Section

**Synthesis and Characterization.** Benzyl bromides were synthesized by a straightforward *N*-bromosuccinimide (NBS) bromination of the commercially available toluene derivatives adapted from the literature.[18] It should be remembered to exert caution when dealing with these materials as benzyl bromides are potent lachrymators. In the case of 2-methyl-3-nitrobenzotrifluoride the reaction required more than 10 times the amount of benzoyl peroxide (reaction may be sterically inhibited) needed for the other brominations. 2,6-Dinitrobenzyl alcohol was prepared as previously described.[5,6,7] 2-Nitro-4-(trifluoromethyl)benzyl alcohol was prepared by reduction of the commercially available acid using a $BH_3$–THF reduction[19] procedure adapted from the literature for similar compounds. The silver salts of pentafluorobenzenesulfonic acid and tresic acid were prepared by hydrolysis of the commercially available acid chlorides followed by reaction of the acid with silver carbonate. The diphenyliodonium and triphenylsulfonium salts of tresic acid were prepared by adapting the synthetic procedure for similar compounds.[20]

The 2-nitrobenzyl esters were prepared by using one of two possible routes (Scheme I) as previously reported.[5-7] One detailed procedure for each of these routes follows, and the summary of reaction conditions and spectroscopic characterization data for all of the esters synthesized can be found in Tables I–III.

2-Methyl-2-nitrobenzotrifluoride, and 2-methyl-3-nitrobenzotrifluoride were obtained from PCR Inc.; 2,2,2-trifluoroethanesulfonyl chloride was obtained from Fluka, and 4-(trifluoromethyl)benzenesulfonyl chloride, 2-(trifluoromethyl)benzenesulfonyl chloride, and 3-(trifluoromethyl)benzenesulfonyl chloride were obtained from Lancaster Chemicals. All other chemicals were obtained from the Aldrich Chemical Co. Poly([(*tert*-butyloxycarbonyl)oxy]styrenesulfone) (3:1, $M_w$ = 150 000, $D$ = 1.9) was synthesized as previously described.[21]

**Synthesis of Silver Tresylate.** To 25 mL of distilled water was added 2,2,2-trifluoroethanesulfonyl chloride (4.30 mL, 39.35 mmol). The two-phase mixture was allowed to stir for 6 h at room temperature until a single phase was obtained. The solution was then put under vacuum overnight to remove HCl ($AgNO_3$(aq) test) and most of the water. This gave 7.6 g of wet acid. The wet acid was then redissolved in 25 mL of distilled water, and silver carbonate was added to the solution until effervescence ceased, and additional silver carbonate no longer dissolved (~10 g silver carbonate added). The neutral solution was filtered to remove the unreacted silver carbonate. The filtrate was dried under vacuum in the presence of $P_2O_5$ to give 10.63 g (99% yield) of silver tresylate, which was used without further purification. Anal. Calcd: C 8.88, H 0.74, S 11.85, F 21.11. Found: C 8.73, H 0.59, S 11.42, F 21.56. $^1$H NMR (ppm, $CD_3CN$) 3.52 (q, $J_{CF}$ = 10.5 Hz, 2 H).

**Synthesis of Silver Pentafluorobenzenesulfonate.** Silver pentafluorobenzenesulfonate was synthesized in a fashion similar to that given above, starting with pentafluorobenzenesulfonyl chloride. In this case, the reaction mixture was heated at reflux for 3 h to ensure complete hydrolysis. The workup was as described above for silver tresylate (99% yield). Anal. Calcd: C 20.28, F 26.76, S 9.01. Found: C 19.96, F 26.66, S 9.57.

**Synthesis of Diphenyliodonium Tresylate.** To a solution of silver tresylate (10.63 g, 39.24 mmol) in 18 mL of distilled water was added diphenyliodonium chloride (12.38 g, 29.24 mmol) suspended in 50 mL of methylene chloride. Upon mixing, silver chloride started to precipitate, and the reaction mixture was stirred at room temperature for 4 h. The two-phase system was then filtered to remove silver chloride. The filtrate was separated into aqueous and organic phases; the aqueous phase was extracted several times with 10-mL aliquots of methylene chloride. The combined extracts were then dried with anhydrous $MgSO_4$, filtered, and stripped of solvent. The crude product was recrystallized twice from $CH_2Cl_2$/ether and dried under vacuum in the presence of $P_2O_5$ to give 9.5 g (77% yield) of white crystals (mp 116–117 °C). Anal. Calcd: C 37.85, H 2.72, S 7.22, I 28.56. Found: C 37.79, H 2.83, S 7.74, I 28.84. $^1$H NMR (ppm, DMSO-$d_6$) 8.02 (d, 4 H), 7.60–7.16 (m, 6 H), 3.03 (q, $J_{HF}$ = 12 Hz, 2 H); IR (cm$^{-1}$, film on NaCl) 1300, 1210, 1140, 1050, 730.

**Synthesis of Triphenylsulfonium Tresylate.** To diphenyliodonium tresylate (4.80 g, 10.81 mmol) was added, under argon, diphenyl sulfide (2.01 g, 1.80 mL, 10.81 mmol) and copper benzoate (0.081 g). This mixture was heated to 130 °C with stirring for 3 h. The reaction mixture was cooled, and the oil obtained was triturated several times with ether. The oily residue was dissolved in 10 mL of distilled water and filtered, and the filtrate was extracted several times with 20-mL aliquots of methylene chloride. The combined organic extracts were dried with anhydrous $MgSO_4$, filtered, and stripped of solvent. The residue thus obtained was dried under vacuum in the presence of $P_2O_5$ overnight to give 3.28 g (~77% yield) of triphenyl-

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**Table I. Synthetic and Spectral Data of 2-Nitrobenzyl Sulfonate Ester Derivatives**

| compd[a] | | % yield | synth method[d] | mp,[e] °C | $^1$H NMR, ppm | IR,[j] cm$^{-1}$ | elem anal. | |
|---|---|---|---|---|---|---|---|---|
| $R_a$ | $R_b$ | | | | | | calcd | found |
| 6-$NO_2$ | 9-$CF_3$ | 48 | Cl, RT = 3 h | 132 | 8.21–7.60 (m, 7 H); 5.69 (s, 2 H)[f] | 1520, 1420, 1300, 1140, 1060, 940 | C: 41.38<br>H: 2.22<br>N: 6.90 | 41.57<br>2.23<br>6.92 |
| 6-$NO_2$ | 10-$CF_3$ | 69 | Cl, RT = 2 h | 99 | 8.33–7.60 (m, 7 H); 5.66 (s, 24)[f] | 1520, 1430, 1345, 1180, 940, 780 | C: 41.38<br>H: 2.22<br>N: 6.90 | 41.45<br>2.15<br>6.87 |
| 6-$NO_2$ | 11-$CF_3$ | 38 | Cl, RT = 17 h | 123 | 8.44–7.26 (m, 7 H); 5.63 (s, 2 H)[f] | 1520, 1370, 1160, 1120, 950, 830, 790, 650 | C: 41.38<br>H: 2.22<br>N: 6.40<br>S: 7.88 | 41.44<br>2.19<br>6.88<br>8.18 |
| 6-$NO_2$ | 11-F | 62 | Cl, RT = 17 h | 139 | 8.29–7.52 (m, 5 H); 7.24 (m, 2 H),[g] 5.58 (s, 2 H) | 1520, 1345, 1180, 960, 750 | C: 43.82<br>H: 2.53<br>H: 7.87<br>F: 5.34 | 43.74<br>2.51<br>7.84<br>5.38 |
| 6-$NO_2$ | 9, 11 di-F | 58 | Cl, RT = 4 h | 115 | 8.20–7.90 (m, 2 H); 7.84–7.52 (m, 2 H),[f] 7.20–6.80 (m, 2 H); 5.70 (s, 2 H) | 1580, 1520, 1350, 1270, 1160, 1150, 1060, 950, 850, 820, 760 | C: 41.60<br>H: 2.15<br>H: 7.48<br>F: 10.15 | 41.74<br>2.22<br>7.70<br>10.06 |
| 6-$NO_2$ | 10-$SO_3R$[b] | 50 | Cl, RT = 4 h | 169d | 8.23–8.19 (m, 7 H); 7.91 (t (8 H), 1 H),[g] 7.81 (t (8 Hz), 2 H); 5.60 (s, 4 H) | 1584, 1552, 1461, 1421, 1382, 1198, 1088, 996, 897, 823, 888, 748, 729 | C: 40.14<br>H: 2.36<br>N: 9.36<br>S: 10.71 | 40.19<br>2.35<br>9.14<br>10.79 |
| 6-$NO_2$ | tresyl[c] | 52 | Ag, RT = 48 h | 103 | 8.20–7.71 (m, 3 H); 5.81 (s, 2 H),[h] 3.90 (q ($J_{HF}$ = 8 Hz), 2 H) | 2980, 1540, 1305, 1195, 950 | C: 31.34<br>H: 2.03<br>N: 8.14 | 31.80<br>2.09<br>7.90 |
| 6-$NO_2$ | 2-$NO_2$ | 66 | Cl, RT = 4 h | 159d | 8.32–7.51 (m, 7 H); 5.67 (s, 2 H)[f] | 1520, 1350, 1370, 1180, 940 | C: 40.73<br>H: 2.35<br>N: 10.97<br>S: 8.36 | 40.65<br>2.34<br>10.80<br>8.71 |
| 6-$CF_3$ | 11-$CH_3$ | 80 | Ag, RT = 17 h, reflux | 85 | 8.00–7.56 (m, 5 H); 7.35 (d (8 Hz); 2 H),[f] 5.43 (s, 2 H); 2.46 (s, 3 H) | 1565, 1520, 1420, 1350, 1170, 1110, 1080, 960, 890, 850, 810, 770, 740, 690, 670, 620 | C: 48.00<br>H: 3.20<br>N: 3.73<br>F: 15.19 | 47.98<br>3.30<br>3.70<br>15.24 |
| 5-$CF_3$ | 11-$CH_3$ | 61 | Ag, RT = 17 h | 110 | 8.26–7.20 (m, 7 H); 5.50 (s, 2 H),[f] 2.45 (s, 3 H) | 1560, 1520, 1430, 1340, 1170, 1115, 1070, 970, 880, 010 | C: 48.00<br>H: 3.20<br>N: 3.73<br>S: 15.19 | 47.93<br>3.09<br>3.68<br>15.20 |
| 4-$CF_3$ | 11-$CH_3$ | 65 | Cl, RT = 17 h | 85 | 8.20–7.70 (m, 2 H); 7.76 (m, 1 H),[f] 5.66 (s, 2 H); 2.46 (s, 3 H) | 1520, 1320, 1160, 1120, 1090, 960, 900, 805, 760 | C: 48.00<br>H: 3.20<br>N: 3.73<br>S: 15.19 | 47.86<br>3.21<br>3.71<br>15.10 |
| 6-$CF_3$ | tresyl[c] | 34 | Ag, RT = 48 h | 84 | 8.00–7.36 (M, 3 H); 5.48 (d, 2 H),[f] 3.86 (9 ($d_{HF}$, 8 Hz), 2 H) | 1560, 1520, 1420, 1360, 1100, 1050, 940 | C: 32.69<br>H: 1.91<br>N: 3.81 | 32.66<br>1.92<br>3.75 |
| 6-$CF_3$ | penta-F | 14 | Ag, RT = 48 h, reflux | 79 | 8.31 (S, 1 H); 7.95 (m, 2 H),[f] 7.83 (d (2 Hz), 2 H); 7.38 (d (2 Hz), 2 H); 5.53 (s, 2 H); 2.46 (s, 3 H) | 1500, 1350, 1300, 1170, 1120, 1100, 990, 940 860, 805 | C: 37.27<br>H: 1.12<br>N: 3.10<br>F: 33.68 | 39.02<br>1.51<br>3.09<br>33.17 |
| 6-F | 11-$CH_3$ | 86 | Ag, RT = 17 h | 75 | 7.82–7.28 (m, 7 H); 5.41 (d ($J_{HF}$ = 1.2 Hz, 2 H),[f] 2.44 (s, 3 H) | 1525, 1350, 1185, 960 | C: 51.69<br>H: 3.69<br>N: 4.31 | 51.80<br>3.64<br>4.36 |
| 6-Br | 11-$CH_3$ | 38 | Ag, RT = 17 h | 112 | 7.84–7.60 (m, 4 H); 7.40–7.28 (m, 3 H),[f] 5.46 (s, 2 H); 2.45 (s, 3 H) | 1520, 1490, 1350, 1160, 1080, 930, 800, 780 | C: 43.53<br>H: 3.13<br>N: 3.63<br>Br: 20.68 | 43.53<br>3.12<br>3.61<br>20.36 |

[a] See Figure 1 for structure. [b] R = 2,6-dinitrobenzyl [c] Ester of tresic acid. [d] Cl = sulfonyl chloride route, Ag = silver sulfonate route, RT = reaction time. [e] Taken from maximum of DSC endothermic peak. [f] $CDCl_3$. [g] Acetone-$d_6$. [h] THF-$d_8$. [i] DMSO-$d_6$. [j] Cast on NaCl.

sulfonium tresylate contaminated with a slight amount of water. Anal. Calcd: C 56.31, H 4.01, S 15.03. Found: C 55.61, H 3.88, S 15.35). $^1$H NMR (ppm, DMSO-$d_6$) 8.00–7.60 (m, 5 H), 3.33 (q, $J_{HF}$ = 12 Hz, 2 H); IR (cm$^{-1}$, film on NaCl) 1430, 1400, 1200, 1090, 1050, 840, 745, 675.

**Synthesis of 2-Nitro-6-(trifluoromethyl)benzyl Bromide.** To a solution of 2-methyl-3-nitrobenzotrifluoride (10.00 g, 48.77 mmol) in 250 mL of $CCl_4$ was added *N*-bromosuccinimide (17.36 g, 97.55 mmol) and benzoyl peroxide (1.18 g). This mixture was heated under reflux for 2 days, after which time $^1$H NMR indicated that only ~10% bromination had occurred. After the solution was filtered, a large excess of benzoyl peroxide was added (11.8 g) along with additional *N*-bromosuccinimide (17.36 g). After 3 more days of stirring under reflux, bromination was almost complete ($^1$H NMR). The solution was filtered to remove excess *N*-bromosuccinimide and succinimide and was stripped of solvent under vacuum. The residue was chromatographed over silica gel with hexane as the eluant. After this dried under vacuum, 9.31 g (75% yield) of a yellowish oil was recovered. Anal. Calcd: C 34.51, H 1.76, N 4.93. Found: C 34.36, H 1.74, N 4.90. $^1$H NMR (ppm, $CDCl_3$) 8.01 (m, 2 H), 7.66 (m, 1 H), 4.93 (s, 2 H); IR (cm$^{-1}$) 1530, 1360.

**Synthesis of 2-Nitro-5-(trifluoromethyl)benzyl Bromide.** The procedure was the same as above except that 1.18 g of benzoyl peroxide was used during the second addition of reagents instead of a large excess. The workup was as described above to give a yellow oil in 54% yield. Anal. Calcd: C 33.80, H 1.76, N 4.93. Found: C 33.85, H 1.89, N 4.99. $^1$H NMR (ppm, $CDCl_3$) 8.14–7.17 (m, 3 H), 4.79 (s, 2 H); IR (cm$^{-1}$, film on NaCl) 3020, 1570, 1510, 1395, 1304, 1160, 1120, 895, 825.

**Synthesis of 2-Nitro-6-fluorobenzyl Bromide.** The procedure was the same as for 2-nitro-6-(trifluoromethyl)benzyl

**Table II. $^{13}$C NMR Spectra Data of 2-Nitrobenzyl Sulfonate Ester Derivatives**

| compd[a] | | carbon assignments,[b] ppm | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $R_a$ | $R_b$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | $R_a$ | $R_b$ |
| 6-$NO_2$[c] | 9-$CF_3$ | 122.65 | 151.58 | 129.9 | 133.05 | | | 64.14 | 131.27 | 130.10 | 129.90 | 135.86 | 134.01 | 133.16 | | 122.41 ($CF_3$) |
| 6-$NO_2$[c] | 10-$CF_3$ | 122.05 | 150.61 | 128.50 | 130.34 | | | 62.62 | 136.30 | 125.03 | 132.07 | 131.31 | 131.41 | 131.21 | | 122.46 ($CF_3$) |
| 6-$NO_2$[c] | 11-$CF_3$ | 122.86 | 150.61 | 128.39 | 131.32 | | | 62.51 | 138.57 | 128.61 | 126.55 | 135.92 | | | | 122.97 ($CF_3$) |
| 6-$NO_2$[d] | 11-F | 122.97 | 151.58 | 129.69 | 131.75 | | | 63.71 | 132.29 | 132.94 | 117.72 | 166.96 | | | | |
| 6-$NO_2$[c] | 9,11-diF | 122.86 | 159.71 | 128.61 | 131.42 | | | 62.73 | 119.86 | 164.04 | 106.18 | 169.24 | 112.31 | 132.78 | | |
| 6-$NO_2$[d] | 10-$SO_2R$[g] | 121.75 | 150.34 | 128.83 | 130.60 | | | 62.69 | 136.69 | 131.16 | 126.83 | | 126.83 | 132.90 | | |
| 6-$NO_2$[e] | tresyl[h] | 121.95 | 150.45 | 128.35 | 131.38 | | | 62.08 | 51.15 | 121.4 | | | | | | |
| 6-$NO_2$[f] | 2-$NO_2$ | 127.53 | 150.53 | 129.04 | 130.66 | | | 68.58 | 129.04 | 147.68 | 122.32 | 132.40 | 139.12 | 129.91 | | |
| 6-$CF_3$[c] | 11-$CH_3$ | 126.22 | 151.58 | 128.06 | 130.70 | 130.12 | 130.59 | 62.51 | 145.40 | 128.17 | 129.01 | 132.29 | | | 122.70 ($CF_3$) | 21.66 ($CH_3$) |
| 4-$CF_3$[c] | 11-$CH_3$ | 134.77 | 146.70 | 122.54 | 134.72 | 130.77 | 129.91 | 67.50 | 145.72 | 128.06 | 130.23 | 132.51 | | | 122.70 ($CF_3$) | 21.66 ($CH_3$) |
| 5-$CF_3$[c] | 11-$CH_3$ | 131.75 | 148.65 | 125.79 | 126.33 | 135.50 | 26.22 | 67.03 | 145.58 | 127.81 | 129.98 | 131.60 | | | 122.50 ($CF_3$) | 21.42 ($CH_3$) |
| 6-$CF_3$[c] | tresyl[h] | 125.25 | 151.36 | 128.71 | 131.75 | 130.75 | 132.01 | 63.86 | 52.20 | 120.96 | | | | | 122.97 ($CF_3$) | |
| 6-F[c] | 11-$CH_3$ | 116.49 | 149.70 | 120.74 | 131.50 | 120.86 | 161.19 | 60.10 | 145.25 | 128.03 | 129.87 | 132.36 | | | | 21.66 ($CH_3$) |
| 6-Br[c] | 11-$CH_3$ | 139.94 | 151.25 | 123.95 | 131.31 | 137.60 | 127.60 | 66.31 | 145.29 | 128.17 | 129.91 | 132.29 | | | | 21.66 ($CH_3$) |
| 6-$CF_3$[c] | penta-F | 124.81 | 151.36 | 128.71 | 131.75 | 130.77 | 132.24 | 64.46 | 105.52 | ~145 | ~134 | ~138 | | | 122.70 ($CF_3$) | |

[a] See Figure 1 for structure. [b] See Figure 1 for assignments of carbons. [c] $CDCl_3$. [d] Acetone-$d_6$. [e] THF-$d_8$. [f] DMSO-$d_6$. [g] R = 2,6-dinitrobenzyl. [h] Ester of tresic acid.

**Table III. Mass Spectral Data of 2-Nitrobenzyl Sulfonate Ester Derivatives**

| compd[a] | | | |
|---|---|---|---|
| $R_a$ | $R_b$ | MW | fragmentations, *m/e* |
| 6-$NO_2$ | 9-$CF_3$ | 406 | 360 ($M^+ - NO_2$); 197 ($M^+ - CF_3C_6H_4SO_2^\bullet$); 180 ($M^+ - CF_3C_6H_4SO_3^\bullet$) |
| 6-$NO_2$ | 10-$CF_3$ | 406 | 360 ($M^+ - NO_2$); 209 ($CF_3C_6H_4SO_2^+$); 197 ($M^+ - CF_3C_6H_4SO_2^\bullet$); 180 ($M^+ - CF_3C_6H_4SO_2^\bullet$) |
| 6-$NO_2$ | 11-$CF_3$ | 406 | 360 ($M^+ - NO_2$); 209 ($CF_3C_6H_4SO_2^+$); 197 ($M^+ - CF_3C_6H_4SO_2^\bullet$); 180 ($M^+ - CF_3C_6H_4SO_3^\bullet$) |
| 6-$NO_2$ | 11-F | 356 | 310 ($M^+ - NO_2$); 197 ($M^+ - FC_6H_5SO_2^\bullet$); 159 ($FC_6H_4SO_2^+$) |
| 6-$NO_2$ | 9,11-di-F | 370 | 197 ($M^+ - F_2C_6H_3SO_2$); 180 ($M^+ - F_2C_6H_3SO_3^\bullet$); 179 ($M^+ - F_2C_6H_3SO_3H$); 177 ($F_2C_6H_3SO_2^+$) |
| 6-$NO_2$ | 10-$SO_3R$[b] | 598 | 180 ($M^+ - (C_6H_4(SO_3H)_2)$) |
| 6-$NO_2$ | tresyl[c] | 344 | 298 ($M^+ - NO_2$); 197 ($M^+ - CF_3CH_2SO_2^\bullet$); 181 ($M = CF_3CH_2SO_3^\bullet$) |
| 6-$NO_2$ | 2-$NO_2$ | 383 | 337 ($M^+ - NO_2$); 197 ($M^+ - NO_2C_6H_4SO_2^\bullet$); 187 ($NO_2C_6H_4SO_3H^+$), 186 ($NO_2C_6H_4SO_3^+$), 180 ($M^+ - NO_2C_6H_4SO_3^\bullet$) |
| 6-$CF_3$ | 11-$CH_3$ | 375 | 375 ($M^+$); 329 ($M^+ - NO_2$); 265 ($M^+ - NO_2 - SO_2$); 204 ($M^+ - TsO^\bullet$); 203 ($M^+ - TsOH$) |
| 4-$CF_3$ | 11-$CH_3$ | 375 | 375 ($M^+$); 329 ($M^+ - NO_2$); 265 ($M^+ - NO_2 - SO_2$); 204 ($M^+ - TsO^\bullet$); 203 ($M^+ - TsOH$) |
| 5-$CF_3$ | 11-$CH_3$ | 375 | 375 ($M^+$); 329 ($M^+ - NO_2$); 265 ($M^+ - NO_2 - SO_2$); 204 ($M^+ - TsO^\bullet$); 203 ($M^+ - TsOH$) |
| 6-$CF_3$ | tresyl[c] | 367 | 321 ($M^+ - NO_2$); 220 ($M^+ - CF_3CH_2SO_2^\bullet$); 204 ($M^+ - CF_3CH_2SO_3^\bullet$); 203 ($M^+ - CF_3CH_2SO_3H$) |
| 6-$CF_3$ | penta-F | 451 | 451 ($M^+$); 406 ($M^+ - NO_2$); 342 ($M^+ - NO_2 - SO_2$); 204 ($M^+ - C_6F_5SO_3^\bullet$); 203 ($M^+ - C_6F_5SO_3H$) |
| 6-F | 11-$CH_3$ | 325 | 325 ($M^+$); 215 ($M^+ - NO_2 - SO_2$); 154 ($M^+ - TsO^\bullet$); 153 ($M^+ - TsOH$) |
| 6-Br | 11-$CH_3$ | 385, 387 | 341 and 339 ($M^+ - NO_2$); 306 ($M^+ - Br^\bullet$); 231 and 232 ($M^+ - SO_2 - 2NO_2$); 215 and 213 ($M^+ - SO_3 - 2NO_2$) |

[a] See Figure 1 for structure. [b] R = 2,6-dinitrobenzyl. [c] Ester of tresic acid.

bromide, except that 1.8 g of benzoyl peroxide was used during the second addition of reagents instead of a large excess. The workup is as described above for 2-nitro-6-trifluoromethyl bromide to give white crystals in 44% yield (mp 38–42 °C). Anal. Calcd: C 38.03, H 2.14, N 5.98. Found: C 38.15, H 2.21, N 6.04. $^1$H NMR (ppm, $CDCl_3$) 8.11–7.15 (m, 3 H), 4.81 (d, 2 H, $J_{FH}$ = 2 Hz); IR ($cm^{-1}$, film on NaCl) 1530, 1360.

**Synthesis of 2-Nitro-6-bromobenzyl Bromide.** The procedure was that for 2-nitro-6-(trifluoromethyl)benzyl bromide except that 1.18 g of benzoyl peroxide was used during the second addition of reagents instead of a large excess. The workup was as described above to give white crystals in 97% yield (mp 65–66 °C, lit.[22] mp 65.5–66 °C). Anal. Calcd: C 28.47, H 1.69, N 4.75, Br 54.24. Found: C 28.63, H 1.72, N 4.76, Br 54.54. $^1$H NMR (ppm, $CDCl_3$) 7.90 (d, 2 H), 7.27 (t, 1 H), 4.83 (s, 2 H); IR ($cm^{-1}$, film on NaCl) 1530, 1360.

**Synthesis of 2-Nitro-4-(trifluoromethyl)benzyl Alcohol.** To a solution of 2-nitro-4-(trifluoromethyl)toluic acid (1.00 g, 4.25 mmol) in cold THF was added dropwise 9.0 mL (9.0 mmol) of a 1 M solution of $BH_3$–THF. The solution was allowed to come to room temperature and stirred for 12 h. After 1 h of heating at the reflux temperature of THF the solution was cooled in ice, and an excess of dilute HCl was added cautiously. After effervescence ceased, the solution was extracted with methylene chloride, and the organic layer washed twice with sodium bicarbonate solution followed by water and dried over anhydrous $MgSO_4$. After removing the solvent, the residual oil was chromatographed ($CH_2Cl_2$, silica gel) to obtain white crystals (0.80 g, 82% yield). Anal. Calcd: C 43.48, H 2.71, N 6.33. Found: C 43.58, H 2.77, N 6.49. $^1$H NMR (ppm, $CDCl_3$) 8.35 (s, 1 H), 7.97 (m, 2 H), 5.01 (s, 2 H), 2.94 (s, 1 H). IR ($cm^{-1}$, film on NaCl) 3300, 2850, 1610, 1520, 1490, 1400, 1320, 1170, 1120.

**Synthesis of 2-Nitro-6-(trifluoromethyl)benzyl Tosylate.** A solution of the 2-nitro-6-(trifluoromethyl)benzyl bromide (3.00 g, 11.0 mmol) in 12 mL of dry acetonitrile was added dropwise to a solution of silver tosylate (3.08 g, 11.0 mmol) in 57 mL of dry acetonitrile under argon. The reaction mixture was stirred under reflux overnight to give complete reaction. The solution was filtered to remove precipitated silver bromide, stripped of solvent under vacuum, redissolved in methylene chloride, and filtered to remove unreacted silver tosylate. After evaporation of the methylene chloride, the residue was recrystallized three times from hot carbon tetrachloride to give 3.32 g (80% yield) of white crystals (mp 76–77 °C). Spectral data for this compound are summarized in Tables I–III.

(22) Harrington, P. J.; Hegedus, L. S.; *J. Org. Chem.* **1984**, *49*, 2657.

**Synthesis of 2,6-Dinitrobenzyl 4-(Trifluoromethyl)benzenesulfonate.** To a stirred solution of 2,6-dinitrobenzyl alcohol (2.00 g, 10.1 mmol) and 4-(trifluoromethyl)benzenesulfonyl chloride (2.71 g, 11.11 mmol) in 30 mL of dry acetone was added a solution of dicyclohexylamine (2.2 mL, 11.1 mmol) in 15 mL of dry acetone under argon. The reaction temperature was kept between 20 and 15 °C. After addition of the amine, dicyclohexylammonium chloride started to precipitate slowly. After the reaction mixture was allowed to stir overnight at room temperature, the solution was filtered to remove the hydrochloride and the filtrate was stripped of solvents under vacuum. The residue was recrystallized three times by using a carbon tetrachloride/chloroform solvent mixture to give 1.55 g (38% yield) of white crystals (mp 111–112 °C). Spectral data for this compound are summarized in Tables I–III.

**Materials Characterization.** Differential scanning calorimetry (DSC) data for the solid samples were obtained by using a Perkin-Elmer DSC-4 differential scanning calorimeter interfaced with a System 4 micropressor and a TADS Model 3700 data station. All samples were heated from 20 to 450 °C at a heating rate of 10 °C/min. Samples ranged in mass from 1.20 to 2.00 mg and were encapsulated in aluminum pans. All measurements were obtained in ultrahigh-purity (99.999%) $N_2$ with a gas flow rate of 30 $cm^3$/min.

Nuclear magnetic resonance spectra were obtained on a JEOL JMN-FX90Q Fourier transform spectrometer. IR spectra were taken by using a Digilab FTS-60 Fourier transform spectrometer. Mass spectra were obtained on a HP 5995 mass spectrometer with a direct insert probe (DIP) heated to the desired temperature. Elemental analyses were obtained by Galbraith Laboratories Inc., Knoxville, TN.

**Quantum Yield Determination.** The samples for the quantum yield determinations were prepared in the following manner. Poly(methyl methacrylate) (PMMA, 10 wt %) was dissolved in cyclohexanone, and 15 wt % (relative to the polymer) of a 2-nitrobenzyl ester was added. The resulting solutions were coated onto standard silicon, NaCl, or quartz substrates with a Headway Research Spinner (Model EC 101). The PMMA/ester films were baked at 90 °C for 30 min in a convection oven. Film thicknesses were measured with a Nanospec AFT film thickness measurement gauge (Model 010 0180) and were in the range 0.5–0.7 μm. Absorbances of resist films were determined by using a Hewlett-Packard Model 8452A diode array UV spectrophotometer. Pulsed laser exposures were carried out using a Suss Model MA56A contact aligner equipped with a Lambda Physik excimer laser operating at 248 nm. The pulse rate was 100 Hz, and energy deposited at the wafer plane was 13 mW/$cm^2$. The quantum yields of the tosylate esters were determined in PMMA films cast onto NaCl disks. The photochemical reaction was followed by monitoring the decrease in the nitro group absorbance at 1530 $cm^{-1}$ with a Digilab FTS60 FT-IR spectrophotometer. Several measurements were made at different exposure times (doses) that effected between 2 and 20% conversion for each sample. The quantum yields found in PMMA were calculated as described previously,[5-7] and the data obtained are summarized in Table IV. The quantum yields were determined in PMMA matrix in order to simplify the measurement and were assumed to be representative of those in actual TBSS resist matrix. This method for measuring the quantum yield has been previously shown[5,6] to give a quantum yield for the photolysis of 2-nitrobenzaldehyde quite close to values reported in the literature. It is assumed that these quantum yields for 2-nitrobenzyl cleavage are representative of acid production because the 2-nitrobenzyl photochemical rearrangement is well-known to occur with a wide variety of hydroxyl protected compounds,[15] giving effective deprotection of these functionalities upon irradiation. This photochemical rearrangement is also known to have a good tolerance for the presence of other functional groups.[16] Moreover, the quantum yields in Table IV are measured for low conversions (2–20%) as would occur in an actual resist film; under these conditions the further photoreaction of the produced nitrosobenzaldehyde does not significantly reduce the quantum yields measured.

**Lithographic Evaluation.** Photoresist solutions were prepared by dissolving TBSS (1 g) and a 2-nitrobenzyl ester or onium salt (8.4 mol % relative to the polymer's pendant *t*-BOC groups) into cyclohexanone (10 mL). The solutions were filtered through a series of 1.0-, 0.5-, and 0.2-μm Teflon filters (Millipore Inc.). For 2-nitro-6-(trifluoromethyl)benzyl pentafluorobenzenesulfonate based resists, the solution was prepared as above, but using 3-ethoxyethylpropionate (EEP) as solvent, because the use of cyclohexanone led to undesirable reactions, which gave rise to complete film dissolution on development.

Photoresist films were spin coated onto hexamethyldisilazane vapor primed, oxidized silicon substrates and prebaked at 120 °C for 2 min. Resist-coated substrates were exposed as described earlier. Proximity printing was used to generate the exposure response curves and vacuum contact printing was employed for patterning and resolution studies. The irradiated films were postexposure-baked (PEB) at 120 °C for 2 min on a hot plate (15 s for the onium salts). For 2-nitro-6-(trifluoromethyl)benzyl pentafluorobenzenesulfonate based resist solutions both the preexposure bakes and postexposure bakes were limited to 30 s at 115 °C as the use of longer times or higher temperatures led to complete film dissolution on development.

The films were developed in aqueous tetramethylammonium hydroxide (TMAH, 0.18 N) for 30 s and rinsed in distilled water for 15 s. All thickness measurements were obtained on a Nanospec film thickness gauge (Nanometrics, Inc.) or a Dektak Model IIA profilometer. The lithographic data are summarized in Table V.

**Catalytic Chain Length.** Polymer solutions of TBSS containing 1.5 mol % of a 2-nitrobenzyl ester were prepared and spun onto silicon substrates as previously described in the section on lithography. IR spectra were taken of the resist film before and after exposure and PEB. The extent of *t*-BOC group removal was followed by monitoring the carbonyl stretching band at 1756 $cm^{-1}$. The amount of acid in the film was calculated from the quantum yields for ester photolysis. Knowledge of the amount of acid generated, in addition to the extent of *t*-BOC group removal, allowed calculation of the moles of *t*-BOC removed per mole of acid generated (catalytic chain length). The catalytic chain length data for a PEB time of 4 min are summarized in Table V.

**Table IV. Thermal Stability, Absorbance, and Quantum Yields of 2-Nitrobenzyl Sulfonate Derivatives**

| compd[a] | | | | |
|---|---|---|---|---|
| $R_a$ | $R_b$ | $T_{min}$, °C | ABS,[d] μm | Φ |
| 6-$NO_2$ | 9-$CF_3$ | 171 | 0.45 | 0.12 |
| 6-$NO_2$ | 10-$CF_3$ | 175 | 0.44 | 0.15 |
| 6-$NO_2$ | 11-$CF_3$ | 175 | 0.47 | 0.15 |
| 6-$NO_2$ | 11-F | 188 | 0.49 | 0.15 |
| 6-$NO_2$ | 9,11-di-F | 170 | 0.50 | 0.14 |
| 6-$NO_2$ | 10-$SO_3R$[b] | 176 | 0.80 | 0.16 |
| 6-$NO_2$ | 11-$CH_3$ | 204 | 0.45 | 0.16 |
| 6-$NO_2$ | 9-$NO_2$ | 163 | 0.65 | 0.10 |
| 6-$CF_3$ | 11-$CH_3$ | 255 | 0.31 | 0.11 |
| 4-$CF_3$ | 11-$CH_3$ | 152 | 0.39 | 0.05 |
| 5-$CF_3$ | 11-$CH_3$ | 154 | 0.38 | 0.07 |
| 6-$CF_3$ | tresyl[c] | 188 | 0.27 | 0.09 |
| 6-$CF_3$ | penta-F | 177 | 0.23[e] | |
| 6-F | 11-$CH_3$ | 218 | 0.25 | 0.12 |
| 6-Br | 11-$CH_3$ | 247 | 0.32 | 0.10 |
| 6-$NO_2$ | tresyl[c] | 147 | *f* | *f* |
| 6-$NO_2$ | 11-$NO_2$ | 166 | 0.65 | 0.10 |
| 6-$NO_2$ | H | 195 | | |
| 6-$NO_2$ | 11-$OCH_3$ | 208 | | |
| 6-$NO_2$ | penta-F | 134 | *f* | *f* |
| 6-$NO_2$ | 9-$NO_2$, 11-$CF_3$ | 136 | *f* | *f* |
| H | 11-$CH_3$ | 124 | *f* | *f* |
| 4-$NO_2$ | 11-$CH_3$ | 159 | | |
| 5-$OCH_3$ | 11-$CH_3$ | 121 | *f* | *f* |

[a] See Figure 1 for position assignments of $R_a$ and $R_b$. [b] R = 2,6-dinitrobenzyl. [c] Ester of tresic acid. [d] Absorbance per micron of a PBSS film containing 8.4 mol % of photogenerator of acid. [e] Measurement done from film cast from EEP. [f] Measurement could not be done due to instability of film.

## Results and Discussion

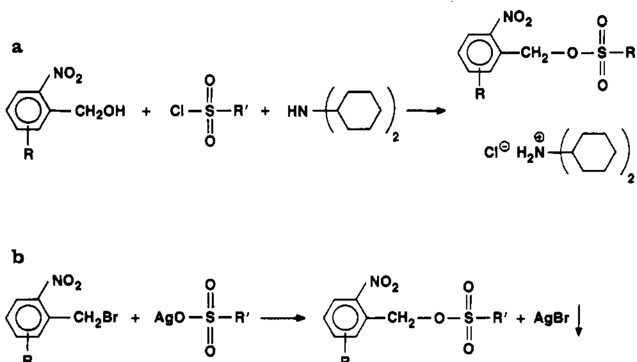
**Materials Synthesis.** The 2-nitrobenzyl esters were synthesized by one of the two routes shown in Scheme I,

**Table V. Lithographic Properties of 2-Nitrobenzyl Sulfonate Ester Derivatives**

| compd[a] $R_a$ | compd[a] $R_b$ | catalytic chain length[d] | sensitivity, mJ/cm² | contrast |
|---|---|---|---|---|
| 6-$NO_2$ | 9-$CF_3$ | 1325 | 8 | >10 |
| 6-$NO_2$ | 10-$CF_3$ | 1820 | 10 | >10 |
| 6-$NO_2$ | 11-$CF_3$ | 797 | 13 | 10 |
| 6-$NO_2$ | 11-F | 554 | 18 | 5 |
| 6-$NO_2$ | 9,11-di-F | 775 | 14 | >10 |
| 6-$NO_2$ | 10-$SO_3R$[b] | 1030 | 8 | 4 |
| 6-$NO_2$ | 9-$NO_2$ | 450 | 17 | 8 |
| 6-$CF_3$ | 11-$CH_3$ | 253[e] | 43 | 10 |
| 4-$CF_3$ | 11-$CH_3$ | 253[e] | 106 | >10 |
| 5-$CF_3$ | 11-$CH_3$ | 253[e] | 65 | 9 |
| 6-$CF_3$ | tresyl[c] | 8490 | 12 | >10 |
| 6-$CF_3$ | penta-F | *f* | 9 | 4 |
| 6-F | 11-$CH_3$ | 253[e] | 72 | 5 |
| 6-Br | 11-$CH_3$ | 253[e] | 72 | 6 |
| 6-$NO_2$ | 11-$NO_2$ | 440 | 17 | 4 |
| 6-$NO_2$ | 11-$CH_3$ | 253 | 25 | >10 |

[a] See Figure 1 for position assignment of $R_a$, $R_b$. [b] R = 2,6-dinitrobenzyl. [c] Ester of tresic acid. [d] PEB = 4 min. [e] Catalytic chain length taken as being the same as the parent tosylate, 2,6-dinitrobenzyl tosylate. [f] Could not be measured due to film instability.

**Scheme I**



and Tables I–III summarize the reaction conditions and characterization data for these compounds.

For the reaction of an acid halide with a benzyl alcohol (Scheme Ia) the reaction time varied from 2 to 24 h. Shorter times were required when the benzenesulfonyl chloride was heavily substituted with electron-withdrawing groups. While such acid chlorides are inherently more reactive, leading to the shorter reaction time, the benzenesulfonate product reacts with dicyclohexylammonium chloride to give exclusive formation of a benzyl chloride derivative. This problem necessitates a quick filtration to remove the salt as soon as the reaction has reached sufficient completion as evidenced by thin layer chromatography. In the reaction of silver sulfonates with benzyl halides (Scheme Ib) the competitive attack by halide is not a problem because of the low solubility of the silver halide. However, this reaction has extremely long reaction times when silver salts of very strong acids (i.e., tresic and pentafluorobenzenesulfonic acid) are employed, presumably because of their low nucleophilicity.[17] This problem can be countered somewhat by heating the reaction mixture to reflux temperature; however, thermal decomposition of the product may then become a competitive process. Representative of this problem is the difference in yields in the synthesis of the 2-nitro-6-(trifluoromethyl)benzyl esters of tosic acid (80% yield) and pentafluorobenzenesulfonic acid (14% yield). All materials prepared have been characterized spectroscopically and by elemental analysis. The results are summarized in Tables I–III. The

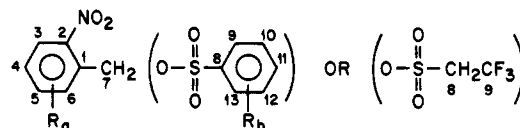
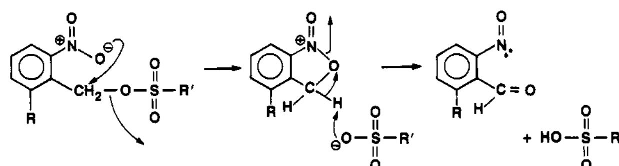


Figure 1. Structural assignment figure for 2-nitrobenzyl sulfonate derivatives.

**Scheme II**



$^{13}C$ NMR spectra (Table II) were assigned on the basis of benzene additivity constants[23] and also from the splitting pattern for coupling interactions with H or F nuclei (in the case of F, the coupling constants were also used[23]). Only two carbons give $^{13}C$ peaks that are characteristic for all the esters; these are the aromatic carbon substituted with the 2-nitro group (~150 ppm) and the benzyl $CH_2$ (~60 ppm) carbon. Figure 1 shows the sequence used in the assignment of the carbons peaks. The $^1H$ NMR spectra (Table I) gave one characteristic peak, a singlet attributed to the $CH_2$ benzyl (~5.5 ppm) proton. Each ester gave three strong IR absorptions (Table I), the $NO_2$ symmetric and asymmetric stretches (~1350, ~1520 $cm^{-1}$) and the $SO_2$ symmetric stretch (~1180 $cm^{-1}$). Common fragments found in the mass spectra (Table III) are ($M^+ - NO_2$), ($M^+ - NO_2 - SO_2$), ($M^+ - O - SO_2 - R$), ($^+SO_2 - R$), where R designates the substituent of the sulfonic acid).

**Thermal Stability.** Scheme II depicts a plausible mechanism that has been previously proposed for the thermal decomposition of the 2-nitrobenzyl sulfonate derivatives.[5,6] This mechanism is similar to one proposed by Dickinson[24] for the decomposition of 2-nitrobenzhydryl tosylate. Thus the thermal stability of 2-nitrobenzyl esters (Table IV) should be governed by substituent effects that could be steric, resonance, or inductive in nature or combinations of all three. To understand which of these factors predominates, the substituent effects for each part of the molecule, the 2-nitrobenzyl chromophore and the masked sulfonic acid, must be considered separately. The effect of changing substituents on the benzenesulfonate moiety was evaluated for a series of 2,6-dinitrobenzyl benzenesulfonate derivatives. The thermal stabilities of these esters, as measured by the minimum in the DSC exotherm ($T_{min}$), range from 134 °C for 2,6-dinitrobenzyl pentafluorobenzenesulfonate[7] to 210 °C for 2,6-dinitrobenzyl 4-methoxybenzenesulfonate[7] (Table IV). In general, the addition of an electron-withdrawing group to the benzenesulfonate moiety leads to increased acidity of the sulfonic acid[25] and decreased thermal stability of the corresponding esters. This trend may be a function of the inductive effect of the particular substituent, an effect that can be confirmed for each derivative by plotting the activation energy for ester decomposition versus the Hammett $\sigma$ constants[26-28] or the sum of $\sigma$ constants in the case

(23) The Sadtler Guide to Carbon-13 NMR Spectra; Simons, W. W., Ed.; Sadtler Research Laboratories Press: Philadelphia, 1983; p 605.
(24) Dickinson, W. B. *J. Am. Chem. Soc.* **1984**, *86*, 3580.
(25) Perrin, D. D.; Dempsey, B.; Serjeant, E. P. *PK$_a$ Predictions for Organic acids and bases*; Chapman and Hall: London, 1981; p 128.
(26) Newman, M. S. *Steric Effects in Organic Chemistry*; John Wiley and Sons: New York, 1956; p 556.
(27) Hansch, C.; Leo, A. *Substituent Constants for Correlation Analysis in Chemistry and Biology*; Wiley-Interscience: New York, 1979; pp 1–12, 69.

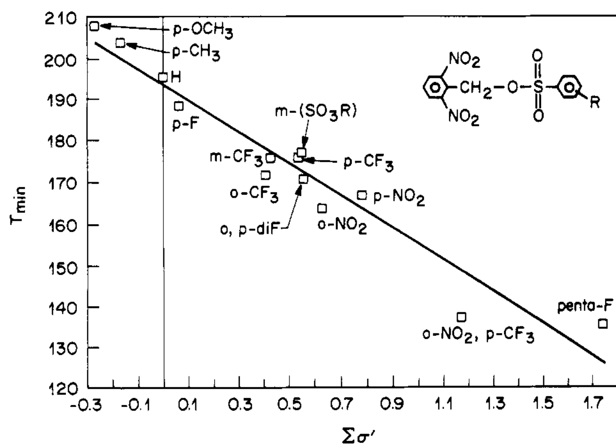



**Figure 2.** Plot of $T_{min}$ versus $\sum\sigma'$ for the 2,6-dinitrobenzyl benzenesulfonate derivatives.

of multiple substitution. Relative values of the activation energy for decomposition of the 2-nitrobenzyl benzenesulfonate derivatives can be obtained from the DSC data ($T_{min}$) assuming the heating rate in the DSC experiments is constant, the kinetics are first order, and the value of the Arrhenius preexponential constants are unchanged over the entire series of esters.

A reasonable tendency toward a linear relationship (for this type of correlation) between $T_{min}$ and the $\sigma$ constants[27] for each substituent (or sum of $\sigma$ constants in the case of multiple substitution) on the benzenesulfonate group was seen. However, the compounds having ortho substituents deviated from the line. This is not unexpected because of steric factors.[26-28] For the 2,6-dinitrobenzyl benzenesulfonate derivatives, the steric effects of the substituents on the benzenesulfonate moiety are unlikely to interfere directly with the nucleophilic attack of the nitro group oxygen (Scheme II) because of their remoteness from the reaction site. However, steric effects can perturb the resonance interaction of a substituent to affect incipient negative charge formation at the sulfur oxygen of the leaving benzenesulfonate group. Therefore, it is important to know the values of the polar effects under sterically difficult conditions. Attempts have been made to separate the inductive, resonance, and steric contributions to the $\sigma$ value.[26] It has been shown that except in the case of extremely electronegative substituents, $\sigma$-p can be used to approximate the value of the polar effects (resonance + inductive) at the ortho position ($\sigma^*$-o) because in the majority of cases, both resonance and inductive effects are the same at these two positions.[26] Furthermore, it is also possible to calculate the value of the inductive contribution ($\sigma'$) to the polar effect for a variety of substituents.[26] Since it is known that steric bulk at the ortho position can hinder or prevent resonance interactions[26] making inductive effects the only contributors to the polar $\sigma$ value, $\sigma'$ was used in those cases where derivatives had ortho substitution at the benzenesulfonate moiety. A plot of $T_{min}$ (for the 2,6-dinitrobenzyl benzenesulfonate derivatives) versus $\sigma$ using these $\sigma'$ values when needed (Figure 2) afforded a reasonable empirical relationship with less deviation from linearity for derivatives with ortho substituents. As expected, attempts to incorporate steric effects into this plot did not improve the linearity, presumably because of the remoteness of the reaction site from the source of steric interaction.

The effect of changing the substituent on the 2-nitrobenzyl chromophore was determined for a series of tosylate esters. The thermal stability of these materials ranged from 124 °C for 2-nitrobenzyl tosylate[5,6] to 255 °C for 2-nitro-6-(trifluoromethyl)benzyl tosylate. Importantly, the thermal stability of the latter ester represents a gain of 50 °C over that for 2,6-dinitrobenzyl tosylate.[5,6] In contrast, the 5-$CF_3$ and 4-$CF_3$ isomers of trifluoromethyl-2-nitrobenzyl tosylate are much less stable than the 6-$CF_3$ isomer, with decomposition temperatures of only 154 and 152 °C, respectively. Thus, resonance effects do not appear to be predominant in determining thermal stability, since such effects would dictate that the 4-$CF_3$ isomer would be more stable than the 5-$CF_3$ analogue. Conversely, if a strong inductive effect were present, a 5-$CF_3$ substituent should result in an ester that is more stable than the corresponding 4-isomer. However, in the 6-$CF_3$ case, where the substituent is attached adjacent to the site of reaction, it is conceivable that even a relatively weak inductive effect could still be of importance in determining thermal stability. To understand the relative importance of this effect versus possible steric factors, different substituents with varying steric bulk and electronegativity were examined. The addition of a fluorine atom, which has a strong electronic effect but is sterically small, gives some enhancement of thermal stability but significantly less than that seen for $CF_3$ substitution (Table IV). Furthermore, substitution with Br, a sterically bulky substituent that has a weaker electronic effect, gives an ester with almost equivalent thermal stability as the $CF_3$ (Table IV) material. Thus, although both steric and inductive effects appear to affect the thermal stability in these esters, the steric factors dominate.

A plot of $T_{min}$ versus the substituent $\sigma$ values[27] showed significant deviations from linearity for those compounds with substituents in the 6-position (ortho). While the inductive polar effect, $\sigma'$, can be used to estimate the polar contribution of substituents at the ortho position under conditions of steric hindrance,[26] for substitution at the 6-position of the 2-nitrobenzyl moiety, the site of reaction is very close to the site of steric hindrance. Thus, it would be expected that in this case, steric factors should directly contribute to the value of the effective $\sigma$ parameter. The Taft steric parameter, Es, has been reported as a measure of steric bulk in Hammett-like plots.[27] Moreover, Hammett-like plots have been made[26] from the sum of $\sigma^*$ and Es. Unfortunately, the values of Es for substituents such as $NO_2$, $CF_3$, and Br do not correlate with the actual steric bulk of these substituents as measured by the Charton steric parameters[27] ($\nu$). For substituents whose Es values better parallel steric bulk, a linear relationship[27] between Es and $\nu$ has been reported. Using this relationship, Es values were calculated for $NO_2$, $CF_3$, and Br by using reported[27] values of $\nu$. For the nitro group, two values of $\nu$ are possible, depending on the orientation of this group.[27] Since the assumption is being made that resonance is disrupted by steric factors, the orientation perpendicular to the plane of the ring was chosen. The sums of $\sigma'$ and calculated Es values were used in the Hammett plots of $T_{min}$ of 2-nitrobenzyl tosylate derivatives in those cases where ortho substituents were present. Reasonable linearity is obtained (Figure 3) that allows the use of this empirical relationship in predicting ester thermal stability.

Because of the enhancement in thermal stability when the 2-nitro-6-(trifluoromethyl)benzyl protecting group is used, it is possible to synthesize thermally stable esters of more powerful acids than was possible with the 2,6-dinitrobenzyl group. Two esters of particular interest are

(28) Shorter, J. *Correlation Analysis in Organic Chemistry: an Introduction to Linear Free Energy Relationships*; Oxford Clarendon: New York, 1973; p 1.

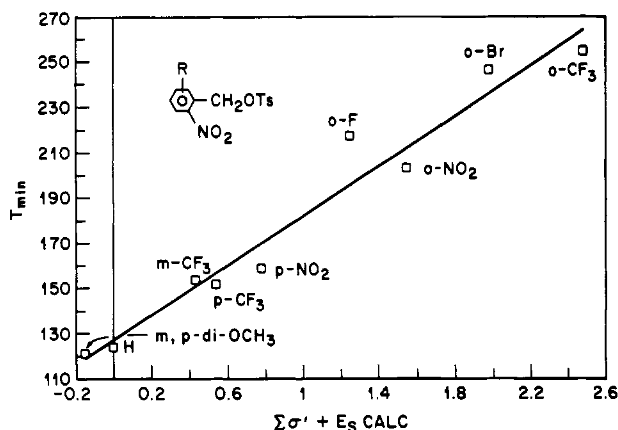



**Figure 3.** Plot of $T_{min}$ versus $\sum\sigma' + E_s$ calc for the 2-nitrobenzyl tosylate derivatives.

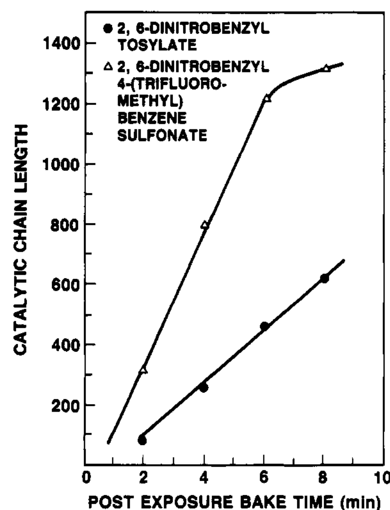



**Figure 4.** Plot of catalytic chain length versus postexposure bake time for representative 2,6-dinitrobenzyl benzenesulfonate derivatives.

those based on tresic acid and pentafluorobenzenesulfonic acid, photogenerators of powerful acids that are useful for chemically amplified resist compositions. The 2,6-dinitrobenzyl esters of these acids had thermal stabilities of only 134 and 147 °C, respectively, as measured by DSC and are therefore incapable of withstanding PEB conditions. However, when 2-nitro-6-(trifluoromethyl)benzyl is used as the photolabile protecting group, both acids form esters having thermal stabilities greater than 175 °C (Table IV). Thus, nitrobenzyl ester based photogenerators of strong acids may be stabilized through appropriate choice of substituent on the benzyl chromophore.

**Quantum Yield.** The quantum yield (Φ) for the photorearrangement of the nitrobenzyl esters in solid poly(methyl methacrylate) matrices varies from 0.05 to 0.16. The efficiency of this reaction appears related to the presence of an ortho substituent on the benzyl moiety. Within experimental error, a change in substituent on the sulfonic acid appendage effects little or no change in Φ (Table IV), but a change in the substitution pattern on the nitrobenzyl portion of the molecule effects significant changes in the quantum efficiency (Table IV). Note that 2-nitrobenzyl esters that lack a second ortho substituent exhibit quantum yields equivalent to that for 2-nitrobenzyl tosylate, ~0.05. Introduction of a trifluoromethyl group or halogen at the 6-position effects an increase in quantum yield to 0.10–0.12, while 2,6-dinitrobenzyl tosylate has a quantum efficiency for photorearrangement of 0.15. Undoubtedly, the 2,6-dinitro analogue exhibits a larger Φ due to an increased probability of reaction that results from the presence of an additional ortho-nitro group. Whether the increased efficiency of photoreaction of the o-$CF_3$, o-F, and o-Br materials results from steric or electronic factors has not been determined. Attempts to correlate these changes with the $\sigma$ parameter or the Es steric parameter for the introduction of substituents onto the molecule did not show any clear relationships.

**Catalytic Chain Length.** In TBSS-based resists formulated with the various esters the extent of deprotection depends not only on the irradiation dose but also on the PEB time. As seen in Figure 4, the extent of the deprotection reaction increases with PEB time for all of the materials examined here, though the rate of this reaction varies with the particular acid employed. Table V shows the catalytic chain length after a PEB of 4 min. The highest values of catalytic chain length are observed for 2-nitro-6-(trifluoromethyl)benzyl tresylate, and the lowest for 2,6-dinitrobenzyl tosylate.

Assuming that the nucleophilicity (probably inversely related to acidity) of the liberated anion determines the extent of *t*-BOC deprotection, it is reasonable to expect a linear relationship between the catalytic chain lengths and the $\sigma$ values of the sulfonate ester substituents. For values of $\sigma \leq 0.4$ the catalytic chain length increases with increasing electron-withdrawing ability of the substituents. However, a further increase in the inductive power of the substituents tends to give unpredictably lower catalytic chain lengths. This may indicate the presence of competitive processes within the polymer matrix in which the photoacid generator is dissolved. One possibility is the reaction of the photoreleased acid on the surface of the resist film with contaminants from the air, e.g., amines. The stronger the acid, the more rapidly this reaction would occur. Recently such surface inhibition has been demonstrated to occur in one of the 2-nitrobenzyl-based resist systems.[29] Further examination of the extent of *t*-BOC deprotection versus benzenesulfonic acid structure is required. The catalytic chain length for the 2-nitro-6-(trifluoromethyl)benzyl pentafluorobenzenesulfonate based resist could not be measured due to the instability of resist films to prolonged and repeated preexposure bakes.

**Optical and Lithiographic Properties.** The lithographic properties sensitivity, contrast, and absorbance of the resists made from TBSS and the 2-nitrobenzyl esters are reported in Tables IV and V. In general the lowest values of absorbance are obtained for resists formulated with esters having electron-withdrawing groups that do not substantially affect the absorbance at 248 nm.

The lithographic sensitivities of the TBSS resists range from 8 to 106 mJ/cm$^2$ for 2,6-dinitrobenzyl 2-(trifluoromethyl)benzenesulfonate and 2-nitro-4-(trifluoromethyl)benzyl tosylate, respectively. Qualitatively higher sensitivities are observed for materials having stronger electron-withdrawing groups attached to the sulfonic acid moiety, especially in the ortho and meta position. This indicates that there is a relationship between inductive effect of a substituent and resist sensitivity.

A plot of lithographic sensitivity versus $\sigma$ values (or $\sigma'$ for ortho substituents) shows that initially the lithographic sensitivity appears to increase with increasing inductive power of the substituent. However, a turnaround appears to occur at a $\sigma$ value of ~0.4. It could be argued that this is an artifact of the differing quantum yields or absorbances for each of the esters. However, plotting the ratio

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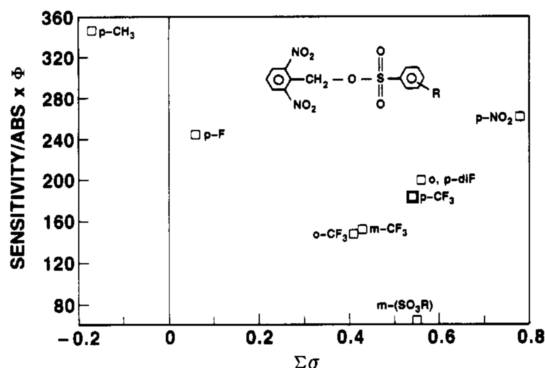


**Figure 5.** Plot of the ratio of lithographic sensitivity and the product of absorbance and quantum yield versus $\sum\sigma$.

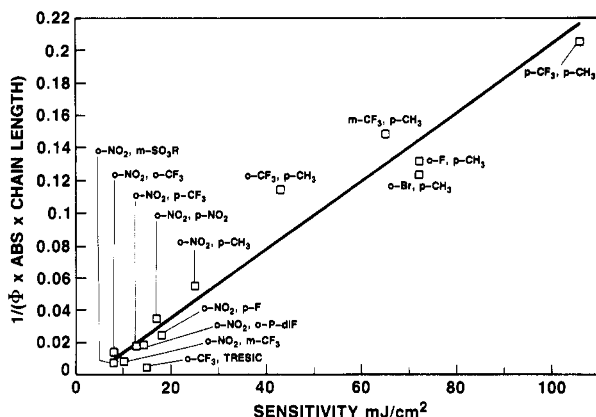


**Figure 6.** Plot of the lithographic sensitivity versus I/(Φ × catalytic chain length × ABS/μm).

of lithographic sensitivity and the product of quantum yield and absorbance per micron versus the σ value shows roughly the same behavior (Figure 5). This parallels the behavior seen for the catalytic chain length (vide infra). Interestingly, bis(2,6-dinitrobenzyl) 1,3-benzenedisulfonate gave the lowest value of this ratio, indicating that it is the most sensitive ester despite the fact that its σ value is far from the maximum.

The 2-nitro-6-(trifluoromethyl)benzyl tresylate ester gave a much lower sensitivity (12 mJ/cm$^2$) than would have been expected on the basis of the acidity, nucleophilicity, and catalytic chain length of the released acids (see following discussion of Figure 6). It is conceivable that contaminants in the ambient air react with the photogenerated acid at the resist–air interface, leading to a decrease in acid concentration and concomitant decrease in resist sensitivity.[29] Moreover, a comparison of the lithographic sensitivities of resists containing the tresylate ester with those found for the resists formulated with the corresponding diphenyliodonium (10 mJ/cm$^2$) or triphenylsulfonium (8 mJ/cm$^2$) tresylate salts shows that the sensitivities of all three resist formulations are similar. The slightly higher sensitivities of resists formulated with the onium salt is not surprising considering that such onium salts generally have higher quantum yields for acid generation. Interestingly, the lithographic sensitivity of the triphenylsulfonium hexafluoroarsenate is 3.4 mJ/cm$^2$, indicating that photogenerated tresic acid does provide access to resist systems approaching the arsenate system in sensitivity.

There are reports in the literature that pentafluorobenzenesulfonate is a better nucleofuge than tresylate,[30-32] and thus the ester based on this acid was expected to give better sensitivity through an increase in the catalytic chain length for *t*-BOC deprotection. Resist solutions prepared in cyclohexanone formulated with 2-nitro-6-(trifluoromethyl)benzyl pentafluorobenzenesulfonate were however found to be unstable to preexposure bake temperatures. Changing the spinning solvent to ethyl ethoxypropionate (EEP) dramatically improved the thermal stability of the resist based upon the pentafluorobenzenesulfonate ester to the point that a lithographic study could be made. However, it should be noted that even here the preexposure bake time was limited in order to prevent premature resist deprotection. Despite this limitation it was found that a resist formulation made from the ester does indeed give a slightly better resist sensitivity (9 mJ/cm$^2$). However, since this measurement was made using EEP as a spinning solvent instead of cyclohexanone, a residual solvent effect cannot be discounted. Although there is a general lowering of the thermal stability of resists formulated with 2-nitrobenzyl sulfonate esters compared to that of the polymer by itself, for all the esters studied lithographically, except in the case of the pentafluorobenzenesulfonate, this effect in not nearly sufficiently pronounced to preclude stability of the resists under standard lithographic process conditions. For instance, no sign of isobutene or carbon dioxide evolution was detected by GC/MS in films of resist made from a variety of *t*-BOC bearing polymers formulated with 2,6-dinitrobenzyl tosylate heated to 120 °C for several minutes.[33] Because of the expected stronger acidity of pentafluorobenzenesulfonic acid, the instability of the pentafluorobenzenesulfonate-based resist may result from the presence of extremely small amounts of this acid in the resist film. Traces of acid could be generated by the reaction of residual solvent with the ester (pentafluorobenzenesulfonate is after all a better leaving group), or it may be already present as a contaminant because of the harsh conditions needed to synthesize the ester. Thus, although there is promise that further resist sensitivity can be achieved by increasing the catalytic chain length of the photoreleased acid further work needs to be done in order to better understand the problem of premature resist deprotection that plagues the pentafluorobenzenesulfonate-based resist.

Previously, it was reported that the clearing dose appeared to be related linearly to the reciprocal of the quantum yield[5,6] for the 2-nitrobenzyl chromophore if the protected acid was kept constant (tosylate esters), and the reciprocal of the catalytic chain length[7] for *t*-BOC deprotection if the chromophore was kept constant (2,6-dinitrobenzyl esters). To test this relationship over a wider range of 2-nitrobenzyl esters having different chromophore and acid moieties, a plot of the reciprocal of the product of quantum yield, catalytic chain length, and absorbance per micron was made versus clearing dose (Figure 6). A reasonably linear plot over the whole range of esters is obtained. However, smaller changes of these three variables are not as well reflected in this plot. Particularly notable is the deviation of the tresic acid ester based resist formulation, which has a lithographic sensitivity far smaller than would have been predicted on the basis of its catalytic chain length for *t*-BOC deprotection, absorbance, and quantum yield. The smaller deviations may stem from experimental errors; however, the larger deviations such as seen for tresic acid may stem from competitive processes

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such as the reaction of basic contaminants in the air with the surface of the resist film (vide infra) that consume acid without leading to removal of a *t*-BOC group. The fact that an unexpected drop in catalytic chain length and lithographic sensitivity has been observed (vide infra) while increasing the acidity of the photoreleased arylsulfonic acids (by increasing the electron-withdrawing ability of substituents) would tend to support this hypothesis as these stronger acids would be more reactive toward basic contaminants. Another possible factor that may be important are the changes of hydrophobicity induced by the introduction of different photogenerators of acid into the resist film. This may govern how quickly impurities from the air can penetrate into the film to react with photogenerated acid.

## Conclusion

A Hammett plot of $T_{min}$ versus the $\sigma$ constants of various groups substituted onto the benzenesulfonate moiety of 2-nitrobenzyl sulfonate esters has shown that the thermal stability of 2-nitrobenzyl esters decreases as the inductive power of substituent groups increases. Thus, increasing the strength of the photochemically released acid decreases the thermal stability of 2-nitrobenzyl sulfonate photogenerators of acid. However, this effect can be countered by the introduction of bulky or inductively electron withdrawing substituents at the 6-position of the 2-nitrobenzyl chromophore. The $CF_3$ group, which is both strongly electron withdrawing and bulky, is particularly effective at stabilization and can enhance the thermal stability of 2-nitrobenzyl ester derivatives by 150 °C over the unsubstituted ester and by 50 °C over the ester with a 2-nitro substituent. This type of approach with even bulkier and more powerful electron-withdrawing groups positioned at the 6-position of 2-nitrobenzyl chromophore could permit the preparation of thermally stable photogenerators of acid incorporating such powerful acids as triflic acid.

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# Bis(*p*-chlorocinnamate) Ester of 2,4-Hexadiyne-1,6-diol: Crystallographic and Spectroscopic Studies of an Unreactive Crystal†

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While the molecular structure of the bis(*p*-chlorocinnamate) ester of 2,4-hexadiyne-1,6-diol (**2**) contains two groups known to be reactive in the solid state, namely, the chlorocinnamoyl and conjugated diyne moieties, the crystal of **2** obtained from chlorobenzene solution is unreactive to $\gamma$-radiation, X-rays, ultraviolet light, and heat at temperatures below its melting point. The crystal of **2** is monoclinic, space group $C2/c$, $a$ = 45.724 (9) Å, $b$ = 8.142 (2) Å, $c$ = 11.336 (3) Å, $\beta$ = 91.66 (3)°, $V$ = 4218.5 (30) Å$^3$, and $Z$ = 8. From the geometry of the unit cell, it is apparent that this phase of **2** is unreactive for structural reasons, as both the chlorocinnamoyl and diyne moieties do not have the preferred intermolecular orientation for solid-state reactivity. Generally similar room-temperature emission spectra were observed for **2** and the reactive *p*-chlorocinnamic acid (**3**). The emission spectra appear to be due to excimers, and the relative energies of the emission spectra correlate with ground-state overlap. A convenient procedure for the photodimerization of **3** to the corresponding truxinic acid (**4**) is reported. Refluxing of **4** with thionyl chloride results in the formation of the cyclic anhydride **5**.

## Introduction

Polydiacetylenes (PDA, **1**) are a class of polymers with conjugated backbones available in the form of macroscopic single crystals.[1] In recent years, we have been interested in the study of chemical,[2,3] thermal,[4,5] photochemical,[6] and magnetic processes[7] whose origin may be traced to specific substituents in the PDA side group and that affect the electronic structure, spectroscopy, and reactivity associated with the conjugated chain.

The reports[8,9] that the photoconductivity action spectrum of the PDA from 1,6-di-*N*-carbazolyl-2,4-hexadiyne (DCH, **1a**) exhibits features that correspond to the maximum of the $S_0$–$S_1$ absorption of the carbazole group and the interpretation[9] that photoconductivity in poly-DCH is associated with charge transfer from the excited carbazole to the conjugated chain raise the following possi-

†This paper is dedicated to Professor Michael Hanack, Universität Tübingen, on the occasion of his sixtieth birthday.

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