Potential photoacid generators based on oxime sulfonates

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Abstract

The bis-oxime of acenaphthenequinone and the mono-oxime of benzil have been sulfonated by reaction with 4-methylbenzenesulfonyl chloride and propylsulfonyl chloride. The four sulfonated oximes were characterised by X-ray single crystal structure determinations. Some photochemical decompositions were studied using a 6 W 254 nm immersion well lamp in dichloromethane. The 4-methylbenzenesulfonate bis-oxime of acenaphthenequinone and the 4-methylbenzenesulfonate mono-oxime of benzil both give 4-methylbenzenesulfonic acid upon irradiation but not 4-methylbenzenesulfinic acid. Fragmentation pathways are discussed. The possible use of these compounds as photoacid generators in polymer resists and the role of secondary reactions to liberate acid is discussed.

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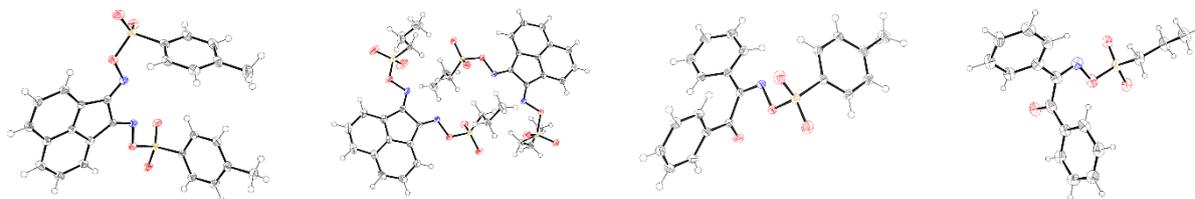
Keywords photoacid generator (PAG), oxime sulfonates, acenaphthenequinone, benzil

Introduction

Improvements in the performance of semiconductor devices arises because of the decreasing size of the features on a silicon chip.[1] Gordon E. Moore, a co-founder of Intel, made the observation in 1965 that circuit densitys of semiconductors would continue to double on a regular basis.[2] This has become known as Moore's Law and it illustrates the astounding developments made in the field (Figure 1).[1]
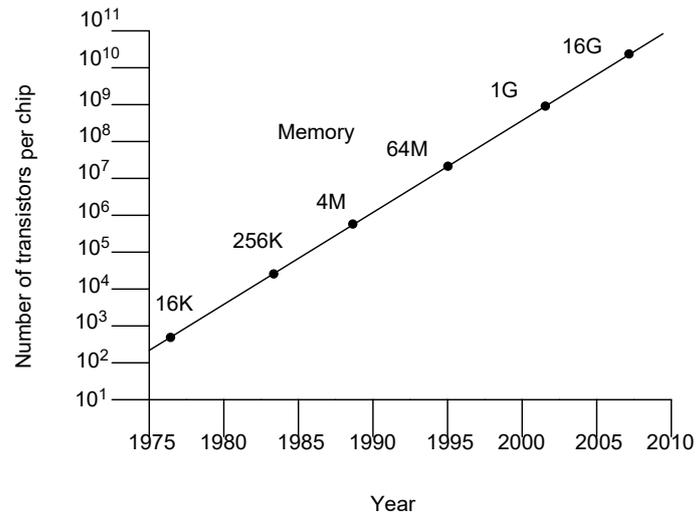
Figure 1 A chart illustrating Moore's Law.

Semiconductor devices or computer chips are fabricated by microlithography (Figure 2).[1] In this technology a radiation sensitive polymer is spin coated and dried, forming a thin film 1-0.1 μm thick, on a single crystal silicon wafer forming a resist. This is irradiated through a mask forming a pattern then the exposed resist films are developed to create images. If the irradiated image is more soluble it is classed as a positive system and if it is less soluble it is classed as a negative system. The remaining resist film serves as a protective layer during etching of the substrate. After etching the remaining resist film is removed leaving behind a circuit pattern. The process is repeated to fabricate complex semiconductor devices.
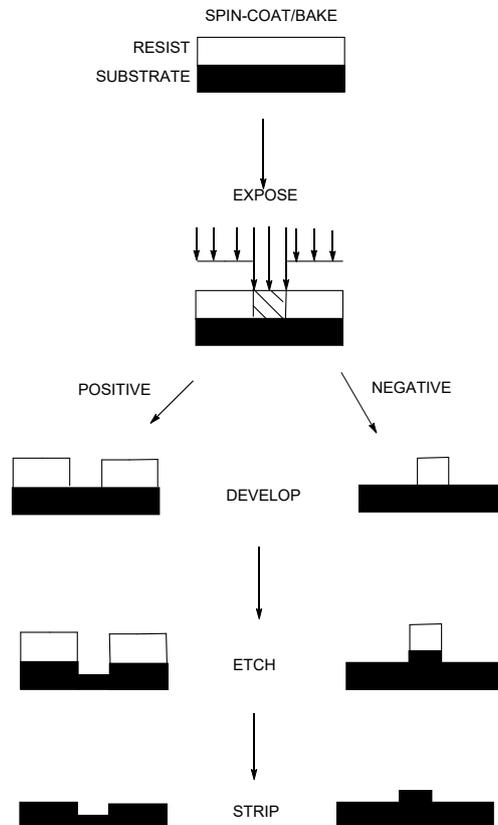
Figure 2 The lithographic imaging process.

The resists contain a light sensitive compound which upon irradiation and development modifys the solubility properties of the resist polymer (Figure 3).[3-4] The success of the semiconductor industry's recent developments has been due to the use of photoacid generators (PAG's) which liberate a small quantity of acid that *catalyses* a chemical reaction in a development step. For example, acid catalysed deprotection of *tert*-butyl esters, liberating isobutene, leaves polymer bound carboxylic acids which solubilise the polymer in aqueous base. Compounds **1** and **2** are likely to liberate the acid of a stable counter-anion[5-7] whereas compounds **3-5** will liberate a sulfonic acid.[3-4,8-11] Decreasing feature size is commensurate with the use of higher energy radiation ranging from the UV (450-190 nm) down to EUV at 7 nm.[3,12-14]
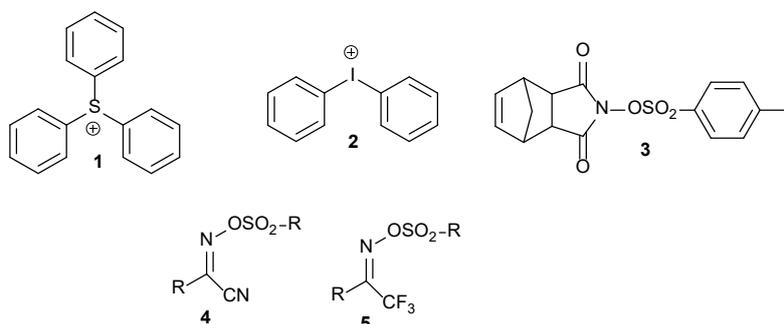
Figure 3 Some representative photoacid generators where R = different alkyl and aryl groups.
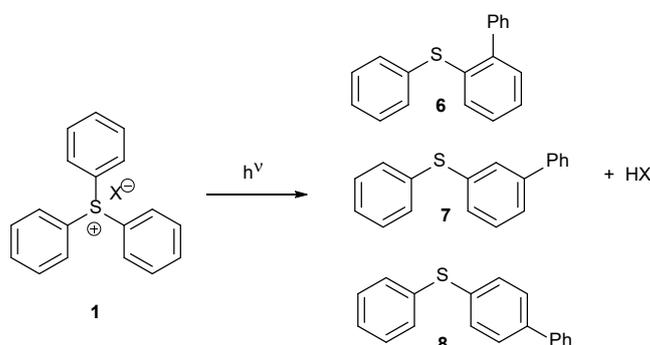
Figure 4 The photochemical fragmentation of a triphenylsulfonium salt to give a phenylthio substituted biaryl and a strong acid.

Figure 4 shows a possible mechanism for the photochemical fragmentation of a Crivello or triarylsulfonium salt.[3] The non-nucleophilic counter-ion becomes the anion of a strong acid HX. A ring proton of the Crivello salt **1** is substituted for the phenyl ring and becomes the proton of the strong acid.

The aim of the project is to develop an understanding of how the class of photoacid generators based on sulfonated oximes can function to modify polymer resists. Some compounds which are representative of literature examples[4,8,10-11] have been prepared, and their photochemical decomposition products studied.

Results and Discussion

The condensation of NH$_2$OH with acenaphthenequinone gives the known bis-oxime **9**[15] and with benzil gives the known mono-oxime **10**[16] only and not a bis-oxime of benzil which is sometimes reported (Figure 5). There are a number of erroneous literature reports claiming that the bis-oxime of benzil can be formed under these conditions.[17-19] Both *syn* and *anti* isomers of benzil derivative **10** have been claimed as they can be separated and the *anti* isomers form metal-ion complexes.[16] We found that compounds **9** and **10** were both sulfonated with either 4-methylbenzenesulfonyl chloride or propylsulfonyl chloride to give compounds **11-14** which are potential photoacid generators (Figure 6). They have been characterised by X-ray single crystal structure determination. The crystal structures show the stereochemistry of these compounds and that of the oximes from which they were made. Only one isomer was formed for each compound **11-14**. Compounds **11** and **12** have both the sulfonate groups pointing away from each other which will arise for steric reasons. However, compounds **13** and **14** are *syn* isomers and are stable. According to the literature the *anti* isomer **15** is unstable during synthesis for stereoelectronic reasons.[16] It is made from the photochemically isolated *anti* oxime.[16] The molecule fragments with the N-OSO$_2$R group *trans* to the C-CO bond. In contrast to this the stability of the *syn* isomers **13** and **14** is striking. The mono-oxime of benzil **10** initially forms as an oil but slowly crystallises to a white solid after a few hours and is a single isomer by ^{1}H and ^{13}C NMR.
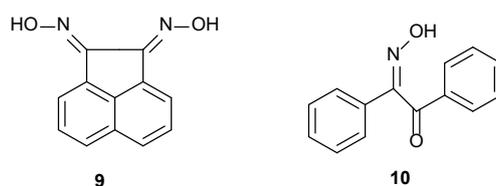
Figure 5 Oximes of acenaphthenequinone **9** and benzil **10**.
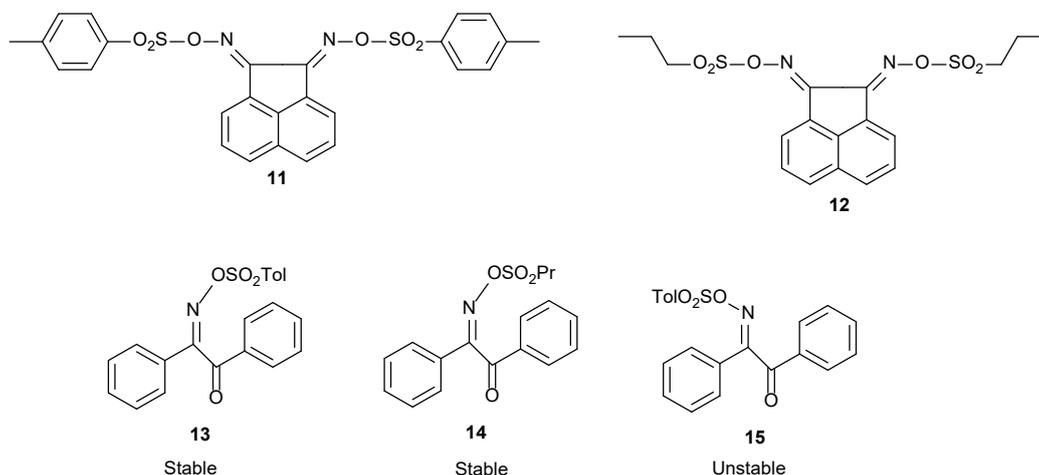
Figure 6 Oxime sulfonates **11-14** characterised by single crystal X-ray structure determinations and a proposed unstable sulfonate **15**.[16]

X-ray single crystal structures

Key geometrical data for **11**–**14** and known oxime sulfonate crystal structures are compiled in Table 1.

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Compound	C–N (Å)	N–O (Å)	C–N–O (°)	N–O–S (°)	C–N–O–S (°)
11 S1 branch	1.2817 (19)	1.4449 (15)	107.20 (11)	111.48 (8)	−176.27 (10)
11 S2 branch	1.2844 (18)	1.4372 (15)	107.88 (11)	111.98 (8)	174.10 (9)
12 S1 branch	1.2828 (18)	1.4380 (14)	108.64 (11)	109.65 (8)	−169.20 (9)
12 S2 branch	1.2846 (17)	1.4427 (13)	108.26 (10)	110.13 (7)	169.22 (9)
12 S3 branch	1.2840 (17)	1.4347 (13)	108.96 (10)	110.23 (7)	−175.69 (8)
12 S4 branch	1.2839 (17)	1.4399 (13)	107.89 (10)	110.99 (7)	−165.68 (9)
13	1.282 (3)	1.459 (2)	108.25 (17)	109.28 (12)	−165.15 (14)
14	1.288 (9)	1.463 (7)	107.3 (6)	110.9 (4)	179.6 (4)
FABWAI[20]	1.281	1.438	109.3	110.3	−176.5
IBUNOI[21]	1.269	1.410	110.0	111.3	175.5
IQOQAG[22]	1.274	1.422	110.2	109.9	−177.4
KEBSIW[23]	1.273	1.415	111.6	109.8	−179.3
KEBSOC[23]	1.269	1.438	111.6	111.1	169.6

Crystallographic Abbreviations: FABWAI = *N,N′-bis*((methylsulfonyl)oxy)-1,2-diphenylethane-1,2-diimine; IBUNOI = (1-(4-bromo-3-(methylsulfanyl)thien-2-yl)-2,2,2-trifluoro-ethaneiminoyl)-*N*-methylsulfonate; IQOQAG = (2,2-dimethyl-6-((trityloxy)methyl)tetrahydrofuro(3,4-d)(1,3)dioxol-4-yl)(((methylsulfonyl)oxy)imino) acetonitrile; KEBSIW = 1-[{[(methylsulfonyl)oxy]imino} (4-nitrophenyl)methyl]pyridin-1-ium trifluoromethanesulfonate; KEBSOC = 1-{*N*-[(methylsulfonyl)oxy]ethanimidoyl}pyridin-1-ium trifluoromethanesulfonate.

Table 1 Comparison of key crystallographic data for oxime sulfonates **11-14**

It may be seen that the C=N and N–O distances of the oxime groups in **11**–**14** and in other known oxime sulfonate crystal structures[20-23] are all very consistent, as are the C=N–O and N–O–S bond angles. The C=N–O–S torsion angles indicate a preference for near planarity for these atoms, which is assumed to be the most stable conformation for oximes[24] and any small deviations might be ascribed to packing forces in the crystal.

In compound **11** (Figure 7) the dihedral angles between the C1–C12 ring system and the pendant C13–C18 and C20–C25 phenyl groups are 81.49 (6)° and 66.93 (6)° respectively. In the crystal of compound **11** the molecules are linked by weak C–H…O interactions.
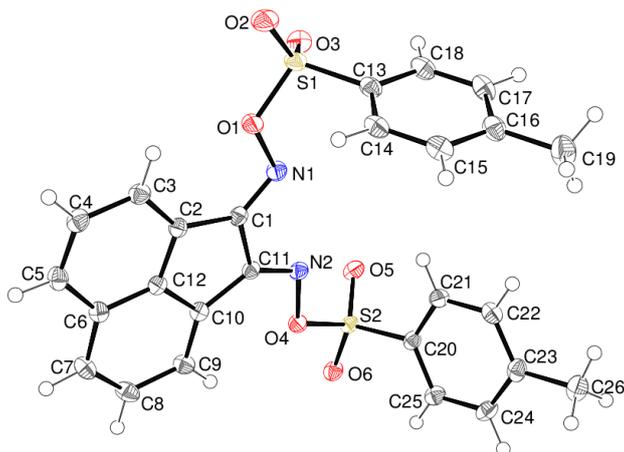
Figure 7 The molecular structure of compound **11** showing 50% displacement ellipsoids.

Compound **12** crystallises with two molecules in the asymmetric unit (Figure 8) with very similar geometries apart from the propyl chains of the sulfonate groups. In the S1 molecule, both of these adopt *anti* conformations [S1–C13–C14–C15 = –178.27 (13)°; C2–C16–C17–C18 = 171.17 (10)°] whereas in the S3 molecule one is *gauche* and one is *anti* [S3–C31–C32–C33 = –60.66 (15)°; S4–C34–C35–C36 = –171.53 (11)°]. In the crystal of compound **12** the molecules are linked by weak C–H…O and C–H…N interactions.
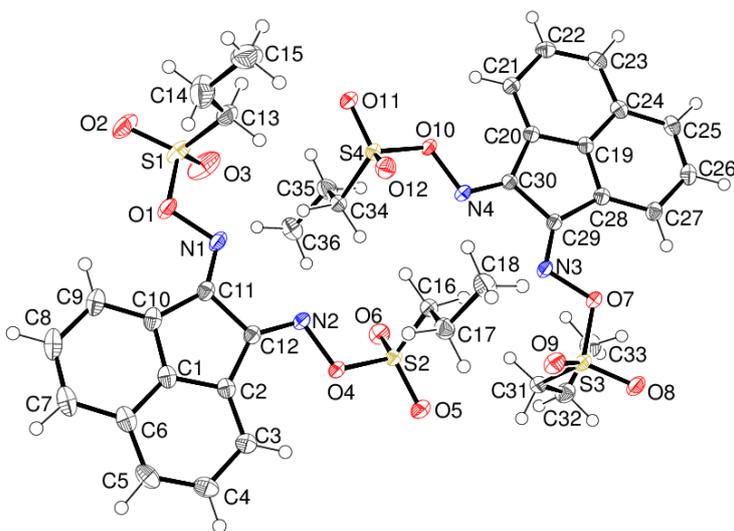
Figure 8 The molecular structure of compound **12** showing 50% displacement ellipsoids.

In compound **13** (Figure 9) the dihedral angles involving the C10–C16 ring (A), the C16–C21 ring (B) and the C1–C6 ring (C) are A/B = 87.28 (11)°, A/C = 50.74 (11)° and B/C = 44.88 (11)°. The N1–C8–C9=O4 torsion angle is –94.6 (2)°. In the crystal of compound **13** the molecules are linked by weak C–H…O interactions.
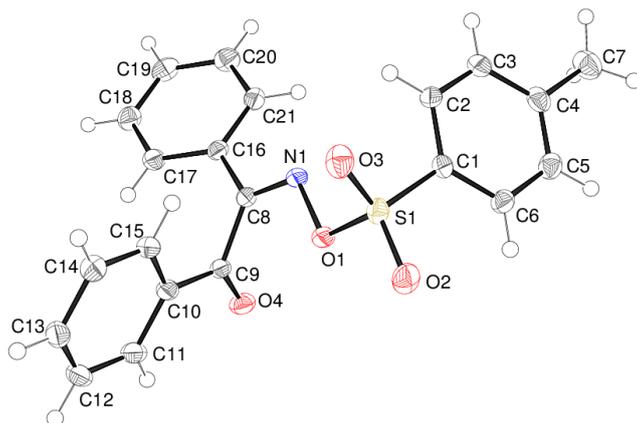
Figure 9 The molecular structure of compound **13** showing 50% displacement ellipsoids.

In compound **14** (Figure 10) the dihedral angle between the C1–C6 and C9–C14 benzene rings is 77.3 (2)° and the propyl chain adopts an extended conformation [S1–C15–C16–C17 = 176.1 (6)°]. In the crystal of compound **14** the molecules are linked by weak C–H…O interactions.
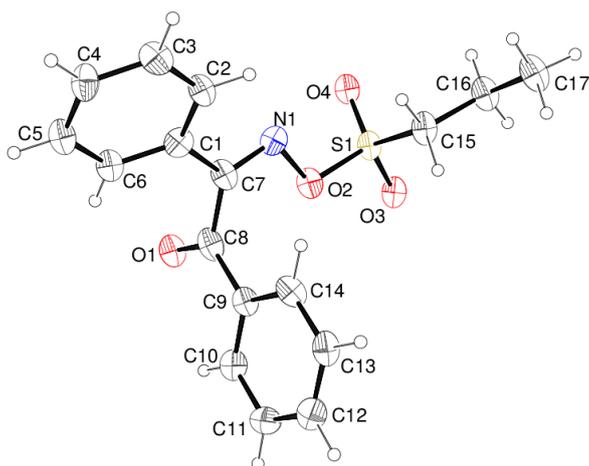
Figure 10 The molecular structure of compound **14** showing 30% displacement ellipsoids.

Photochemical irradiation

Compounds **11** and **13**, representative of many other compounds, [4,8,10-11] were irradiated in CH_2Cl_2 with a 6W 254 nm lamp in a 100 ml immersion well for 5 h. This was done without deoxygenation because some polymer resist films are irradiated in air (365 nm i line, 248 nm KrF laser and 193 nm ArF laser by a dry process). TLC analysis of the mixture after evaporation of the solvent showed that the starting material had been consumed. Figure 11 shows some of the possible fragmentation products **16-19**. These might form by a light catalysed fragmentation of the oxime N-O bond followed by a secondary reaction of the sulfonate radical such as hydrogen abstraction from the solvent (Figure 12). Termination of free radicals after irradiation could also occur by recombination which could give peroxide **22**. This peroxide **22** would require heating, in a develoment step, or hydrolysis to release acid **16**. In these studies only evidence for 4-methylbenzenesulfonic acid **16** has been found. ^{1}H NMR analysis of the crude product in D_2O, from the irradiation of compounds **11** and **13**, showed two strong

aromatic doublets and an upfield singlet which matched the spectrum for the standard 4-methylbenzenesulfonic acid **16**. This assignment was confirmed by comparison of the ^{13}C NMR data with standards of 4-methylbenzenesulfonic acid **16** and 4-methylbenzenesulfinic acid **17**. Again the data matched that for the standard **16** including the chemical shift at 142.3 ppm of the quaternary carbon attached to the sulfur atom. This occurs at a different chemical shift of 150.5 ppm for the sulfinic acid **17**. Compound **13** released acid more efficiently than compound **11** as the ^{1}H NMR data was stronger and cleaner. It was difficult to identify other products from the crude mixtures. However, no nitriles such as compounds **18** or **19**, that might form from radical **20**, were detected by ^{1}H NMR in CD$_3$OD or by the benzonitrile IR stretch at 2228 cm^{-1}. The fate of species **20** is unknown. A water extract of both products turned blue litmus red showing that acid forming precursors were liberated in the photolysis. Light sensitivity is required for applications as photoacid generators making these compounds potentially useful in the field. However, they must also be soluble in appropriate solvents used in the industry such as propylene glycol methyl ether acetate (PGMEA) or ethyl lactate. Although compound **13** is soluble in these solvents compound **11** has poor solubility in them.
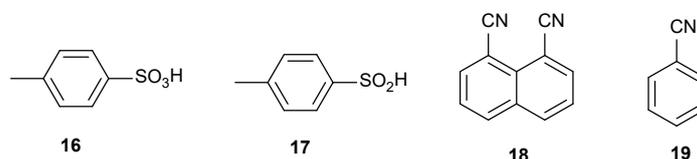
Figure 11 Some possible products from the photochemical decomposition of compound **11** and **13**.
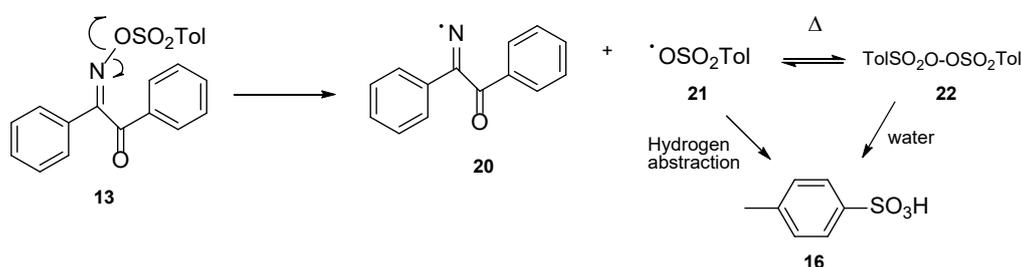
Figure 12 Proposed scheme for the fragmentation of oxime sulfonate **13** to release 4-methylbenzenesulfonic acid **16**.

Conclusion

The crystal structures of compounds **11-14** verifys their oxime stereochemistry. Photochemical decomposition of the representative compounds **11** and **13** gave 4-methylbenzenesulfonic acid **16** which was observed in the ^{1}H NMR and ^{13}C NMR spectrum of the crude product in D$_2$O. Irradiation of both compounds **11** and **13** gave solutions in water that turned blue litmus paper red. This work provides evidence that the class of acid released from the irradiation of oxime sulfonates is a sulfonic acid, which might catalyse modification of a polymer resist during development.[4,8,10-11] Irradiation of compound **11** did not give the expected 1,8-dicarbonitrile **18** and irradiation of compound **13** did not give benzonitrile **19** in easily detectable amounts. The efficient release of acid and good solubility suggests that compound **13** has potential use as a photoacid generator but acid is not liberated directly and requires a secondary hydrogen abstraction step or hydrolysis step.

Experimental

General: IR spectra were recorded on a diamond anvil spectrophotometer. UV spectra were recorded using a Perkin-Elmer Lambda 25 UV-VIS spectrometer with EtOH as the solvent. ^{1}H and ^{13}C NMR spectra were recorded at 600 MHz and 150 MHz respectively, using a Varian 400 spectrometer. Chemical shifts, δ are given in ppm relative to the residual solvent and coupling constants, J are given in Hz. Low resolution and high resolution mass spectra were obtained at the University of Wales, Swansea using electron impact ionisation and chemical ionisation. Melting points were determined on a Kofler hot-stage microscope. Irradiations were done in a 100 ml immersion well with a Photochemical Reactors 6W lamp (Blounts Farm, Blounts Court Road, Sonning Common, Reading, Berkshire, RG4 9PA) and air cooling from a fume hood fan. No water flow was required with DCM as solvent. Reflective foil was used to shield the lamp. The method is user friendly for students.

General procedure for di-oximes or mono-oximes.

Acenaphthylene-1,2-dione di-oxime 9 A literature procedure was followed but the work-up was different.[15] Acenaphthenequinone (5.0 g, 27.5 mmol), hydroxylamine hydrochloride (4.2 g, 60.4 mmol) and sodium acetate (5.0 g, 61 mmol) were stirred at rt in EtOH (150 ml) for 24 h. The mixture was gently refluxed for 2 h then cooled. The mixture was poured into water (400 ml) and left to stand for 2 h as the product precipitated. This was filtered with a large sinter, washed with water (100 ml) and air dried to give the *title compound* (5.2 g, 98%) as an off white solid, mp > 220 °C[14] (from dichloromethane/light petroleum ether 40-60). λ_{max} (EtOH)/nm 325 (log ε 3.2), 232 (4.6) and 212 (4.5); ν_{max}(Diamond) 3453w, 3018w, 2837w, 1489w, 1418w, 1347w, 1289w, 1228w, 1185w, 1146w, 1016m, 1000m, 937m, 854s, 825s, 773s, 611m, 539m and 443s; δ_H(600 MHz; CDCl$_3$) 7.69 (2H, m), 7.97 (2H, d, $J = 6.0$) and 8.43 (2H, d, $J = 6.0$); δ_C(150 MHz; CDCl$_3$) 125.5, 127.1, 127.8, 129.0, 130.6, 136.9 and 149.6; *m/z* (orbitrap ASAP) 213.0659 (M$^+$ + H, 100%) C$_{12}$H$_9$N$_2$O$_2$ requires 213.0659.

Benzil-1,2-dione mono-oxime 10[16] This was made by the same method.

Synthesis of di-oxime and oxime sulfonates
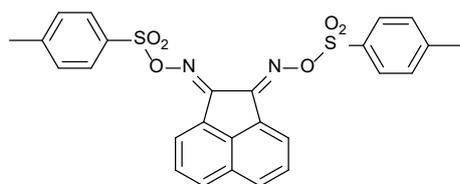
 (1E,2E)-Acenaphthylene-1,2-dione-O,O-ditosyl di-oxime 11 The bis-oxime of acenaphthenequinone **11** (400 mg, 1.9 mmol), 4-methylbenzenesulfonyl chloride (863 mg, 4.5 mmol) and Et$_3$N (457 mg, 4.5 mmol) were stirred in CH$_2$Cl$_2$ (100 ml) for 24 h at rt. The clear organic layer was washed with water (100 ml x 2) and dried over MgSO$_4$. The solution was concentrated *in vacuo* to a solid then extracted 3 times by swirling with light petroleum ether (100 ml) which removed excess 4-methylbenzenesulfonyl chloride. Swirling with a smaller amount of dichloromethane (30 ml) removed brown impurities and gave a product (470 mg, 48%). Proton NMR analysis showed this product to be impure, containing triethylammonium tosylate, so it was dissolved in dichloromethane (300 ml) and extracted with water (100 ml x 3) and concentrated *in vacuo* to give the *title compound* (0.34 g, 35%) as a pale yellow solid, mp > 220 °C (from dichloromethane/light petroleum ether 40-60). λ_{max} (EtOH)/nm 333 (log ε 3.3), 316 (3.3), 245-280sh (3.5) and 229 (4.2); ν_{max}(Diamond) 1596w, 1575w, 1490w, 1390w, 1368w, 1178s, 1093m, 816s, 773s, 685s, 661s, 615s and 458m; δ_H(600 MHz; CDCl$_3$) 2.42 (6H,

s), 7.31 (4H, d, J = 12.0), 7.62 (2H, t, J = 6.0 and 6.0), 7.92-7.95 (6H, m) and 8.33 (2H, d, J = 6.0); δ_C(150 MHz; CDCl$_3$) 21.7, 126.7, 128.4, 128.8, 129.5, 129.7, 130.1, 130.5, 131.8, 138.8, 145.7, 155.2; m/z (orbitrap ASAP) 521.0842 (M$^+$ + H, 100%)   C$_{26}$H$_{21}$N$_2$O$_6$S$_2$ requires 521.0841; 179.0603 (naphthalene-1,8-dicarbonitrile + H, 50%) C$_{12}$H$_7$N$_2$ requires 179.0609
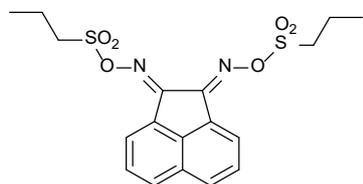
(1E,2E)-Acenaphthylene-1,2-dione-O,O-dipropylsulfonyl di-oxime 12 The bis-oxime of acenaphthenequinone **11** (1.0 g, 4.7 mmol), propanesulfonyl chloride (1.34 g, 9.4 mmol) and Et$_3$N (0.95 g, 9.4 mmol) were stirred in CH$_2$Cl$_2$ (100 ml) for 24 h at rt. The clear organic layer was washed with water (100 ml x 2) and dried over MgSO$_4$. The solution was concentrated *in vacuo* to a solid then extracted by swirling with light petroleum ether (30 ml x 10). Then concentration *in vacuo* gave the *title compound* (0.62 g, 31%) as a pale yellow solid, mp 215-216 °C (from dichloromethane/light petroleum ether 40-60). λ_{max} (EtOH)/nm 331(log ε 4.0), 316(4.1) and 229(4.9); ν_{max}(Diamond) 1687s, 1454w, 1365s, 1227m, 1173s, 948w, 811s, 732s, 683s, 629s, 580s, 539s and 497s; δ_H(600 MHz; CDCl$_3$) 1.17 (6H, t, J = 6.0), 2.04 (4H, h, J = 6.0), 3.58 (4H, t, J = 6.0), 7.77 (2H, t, J = 6.0), 8.11 (2H, d, J = 12.0) and 8.49 (2H, d, J = 6.0); δ_C(150 MHz; CD$_3$OD) 12.8, 17.3, 51.2, 126.7, 128.8, 128.9, 130.5, 130.6, 138.9, 156.0; m/z (orbitrap ASAP) 425.0840 (M$^+$ + H, 100%) C$_{18}$H$_{21}$N$_2$O$_6$S$_2$ requires 425.0840; 179.0606 (naphthalene-1,8-dicarbonitrile + H, 95%) C$_{12}$H$_7$N$_2$ requires 179.0609.
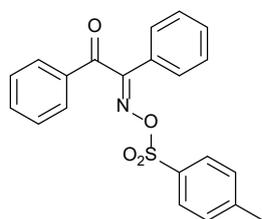
(E)-1,2-Diphenyl-2-((tosyloxy)imino)ethan-1-one 13[16] The mono-oxime of benzil **12** (2.0 g, 8.9 mmol),[15] 4-methylbenzenesulfonyl chloride (3.4 g, 17.8 mmol) and Et$_3$N (2.1 g, 21.0 mmol) were stirred in CH$_2$Cl$_2$ (100 ml) for 24 h at rt. The clear organic layer was washed with water (100 ml x 2) and dried over MgSO$_4$. The solution was concentrated *in vacuo* to an oil which was swirled with light petroleum ether (30 ml x 3) and left to crystallise. The solid was then extracted by swirling with light petroleum ether (30 ml x 7) and concentrated *in vacuo*. The solid was then dissolved in dichloromethane (100 ml) and filtered through a pad of silica to give the *title compound* (1.8 g, 53%) as a pale yellow solid, mp 121-122 °C (from dichloromethane/light petroleum ether 40-60). λ_{max} (EtOH)/nm 256(log ε 4.3), 232 (4.2) and 207(4.6); ν_{max} (Diamond) 1680s, 1594w, 1446w, 1371s, 1230m, 1174s, 1091w, 759s, 719s, 660s, 579s, 545s, 515s and 470m; δ_H(600 MHz; CDCl$_3$) 2.38 (s, 3H), 7.37 (4H, m), 7.48 (3H, m), 7.57 (2H, d, J = 6.0), 7.66 (1H, t, J = 6.0 and 12.0) and 7.85 (4H, t, J = 6.0 and 6.0); δ_C(150 MHz; CDCl$_3$) 21.8, 127.5, 128.9, 129.0, 129.2, 129.3, 129.5, 129.8, 132.2, 132.3, 133.7, 135.2, 145.5, 163.2 and 190.1; m/z (EI) 397.1211 (M$^+$ + NH$_4$, 100%) C$_{21}$H$_{21}$N$_2$O$_4$S requires 397.1217; (orbitrap ASAP) 104. 0519 (benzonitrile + H, 100%) C$_7$H$_6$N requires 104.0500.
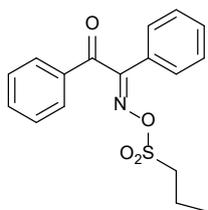
(*E*)-1,2-Diphenyl-2-(((propylsulfonyl)oxy)imino)ethan-1-one 14 The mono-oxime of benzil **12** (1.0 g, 4.2 mmol), propanesulfonyl chloride (1.0 ml, 8.4 mmol) and Et$_3$N (0.85 g, 8.4 mmol) were stirred in CH$_2$Cl$_2$ (100 ml) for 24 h at rt. The clear organic layer was washed with water (100 ml x 2) and dried over MgSO$_4$. The solution was concentrated *in vacuo* to a solid then extracted by swirling with light petroleum ether (30 ml x 10). This gave the *title compound* (1.3 g, 89%) as a colourless solid, mp 126-127 °C (from dichloromethane/light petroleum ether 40-60). λ$_{max}$ (EtOH)/nm 255(log ε 3.7) and 208(4.1); ν$_{max}$(Diamond) 1680s, 1379m, 1367m, 1172s, 841m, 829m, 806s, 796s, 773s, 568s, 519m, 519m and 493m; δ$_H$(600 MHz; CDCl$_3$) 1.09 (3H, t, *J* = 6.0 and 6.0), 1.92 (2H, m), 3.37 (2H, t, *J* = 6.0 and 8.0), 7.45 (2H, t, *J* = 6.0 and 12.0), 7.54 (3H, t, *J* = 6.0 and 12.0), 7.66-7.73 (3H, m) and 7.97 (2H, d, *J* = 12.0); δ$_C$(150 MHz; CDCl$_3$) 12.8, 17.1, 51.2, 127.7, 128.8, 129.3, 129.4, 129.6, 132.5, 133.6, 135.4, 163.9 and 190.0; *m/z* (orbitrap ASAP) 349.1215 (M$^+$ + NH$_4$, 20%). C$_{17}$H$_{21}$N$_2$O$_4$S requires 349.1222.

Photochemical irradiations

200 mg of compounds **11** or **13** were irradiated with a 6W lamp for 5 h in 100 ml of CH$_2$Cl$_2$ without deoxygenation. The solution was concentrated and TLC analysis showed extensive decomposition of the starting material had occurred. The crude products were both shown to contain 4-methylbenzenesulfonic acid **16** by ^{1}H NMR. δ$_H$ (400 MHz; D$_2$O) 2.20 (3H, s), 7.11 (2H, d, *J* = 8.0) and 7.45 (2H, d, *J* = 8.0); δ$_C$ (150 MHz; D$_2$O) 20.4, 125.2, 129.3, 139.3 and 142.3. From the irradiation of compound **11** ν$_{max}$ (diamond anvil) 1678 cm^{-1}; From the irradiation of compound **13** ν$_{max}$ (diamond anvil) 1682 cm^{-1}. Standard of 4-methylbenzenesulfonic acid **16** δ$_H$ (400 MHz; D$_2$O) 2.10 (3H, s), 7.00 (2H, d, *J* = 8.0) and 7.41 (2H, d, *J* = 8.0); δ$_C$ (150 MHz; D$_2$O) 20.4, 125.2, 129.3, 139.3 and 142.3; Standard of 4-methylbenzenesulfinic acid **17** δ$_H$ (400 MHz; D$_2$O) 2.29 (3H, s), 7.27 (2H, d, *J* = 8.0) and 7.46 (2H, d, *J* = 8.0); δ$_C$ (150 MHz; D$_2$O) 20.6, 123.5, 129.6, 141.1 and 150.5.

Crystal structure determinations

Single crystals of **11**–**14** were recrystallised from dichloromethane/light petroleum ether solution. Intensity data for **11**–**14** were collected at *T* = 100 K using a Rigaku AFC11 CCD diffractometer (Mo Kα radiation, λ = 0.71073 Å for **11** and **13** and Cu Kα radiation, λ = 1.54184 Å for **12** and **14**). Each structure was easily solved by direct methods and the structural models were completed and optimised by least-squares refinement against |*F*|^2 using SHELXL-2014.[25] The crystal quality for **14** was notably poorer than for the other structures. For all structures, the H atoms were geometrically placed (C–H = 0.95–0.98 Å) and refined as riding atoms. The methyl groups were allowed to rotate, but not to tip, to best fit the electron density. The constraint U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C) was applied in all cases.

11: C$_{26}$H$_{20}$N$_2$O$_6$S$_2$, M_r = 520.56, pale orange column, 0.23 × 0.06 × 0.05 mm, triclinic, space group *P*$\bar{1}$ (No. 2), *Z* = 2, *a* = 7.9131 (2) Å, *b* = 11.5800 (3) Å, *c* = 14.4677 (3) Å, α = 103.676 (2)°, β = 95.088 (2)°, γ = 109.671 (2)°, *V* = 1192.28 (5) Å^3 at 100 K. Number of measured and unique reflections = 20472 and 5452, respectively (–10 ≤ *h* ≤ 10, –15 ≤ *k* ≤ 15, –18 ≤ *l* ≤ 18; 2θ$_{max}$ = 50.5°; R_{Int} = 0.017). Final *R*(*F*) = 0.035, *wR*(*F*^{2}) = 0.093 for 327 parameters and 4971

reflections with $I > 2\sigma(I)$ (corresponding R-values based on all 5452 reflections = 0.039 and 0.095, respectively), CCDC deposition number 1870464.

12: $C_{18}H_{20}N_2O_6S_2$, M_r = 424.48, pale yellow block, 0.23 × 0.21 × 0.18 mm, triclinic, space group $P\bar{1}$ (No. 2), Z = 4, a = 7.06267 (6) Å, b = 11.08547 (10) Å, c = 25.1261 (2) Å, α = 96.2327 (6)°, β = 90.5797 (8)°, γ = 95.8034 (7)°, V = 1945.10 (3) Å^3 at 100 K. Number of measured and unique reflections = 34798 and 7043, respectively ($-8 \leq h \leq 8$, $-13 \leq k \leq 13$, $-30 \leq l \leq 30$; $2\theta_{max}$ = 136.5°; R_{Int} = 0.015). Final $R(F)$ = 0.029, $wR(F^2)$ = 0.082 for 509 parameters and 6850 reflections with $I > 2\sigma(I)$ (corresponding R-values based on all 7043 reflections = 0.030 and 0.082, respectively), CCDC deposition number 1870465.

13: $C_{21}H_{17}NO_4S$, M_r = 379.42, colourless block, 0.27 × 0.12 × 0.04 mm, monoclinic, space group Ia (No. 9), Z = 4, a = 13.0319 (6) Å, b = 12.1421 (5) Å, c = 11.8439 (5) Å, β = 102.396 (5)°, V = 1830.42 (14) Å^3 at 100 K. Number of measured and unique reflections = 10604 and 3801, respectively ($-16 \leq h \leq 15$, $-15 \leq k \leq 15$, $-15 \leq l \leq 15$; $2\theta_{max}$ = 55.0°; R_{Int} = 0.035). Final $R(F)$ = 0.029, $wR(F^2)$ = 0.076 for 245 parameters and 3610 reflections with $I > 2\sigma(I)$ (corresponding R-values based on all 3801 reflections = 0.031 and 0.077, respectively), Flack absolute structure parameter = 0.02 (4), CCDC deposition number 1870466.

14: $C_{17}H_{17}NO_4S$, M_r = 331.37, colourless needle, 0.30 × 0.03 × 0.01 mm, triclinic, space group $P\bar{1}$ (No. 2), Z = 2, a = 5.2869 (4) Å, b = 9.1995 (12) Å, c = 16.829 (2) Å, α = 97.497 (11)°, β = 95.822 (8)°, γ = 94.282 (9)°, V = 804.11 (16) Å^3 at 100 K. Number of measured and unique reflections = 10351 and 2857, respectively ($-5 \leq h \leq 6$, $-10 \leq k \leq 10$, $-19 \leq l \leq 20$; $2\theta_{max}$ = 135.0°; R_{int} = 0.129). Final $R(F)$ = 0.119, $wR(F^2)$ = 0.307 for 209 parameters and 1982 reflections with $I > 2\sigma(I)$ (corresponding R-values based on all 2857 reflections = 0.158 and 0.338, respectively), CCDC deposition number 1870467.

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