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New Dry Arenediazonium Salts, Stabilized to an Exceptionally High Degree by the Anion of *o*-Benzenedisulfonimide

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Abstract: Arenediazonium *o*-benzenedisulfonimides **3** (20 examples, yield >90%) were prepared in the dry state by diazotization of aromatic amines with *i*-pentyl nitrite and *o*-benzenedisulfonimide in glacial acetic acid or formic acid at $0-5^{\circ}$ C. Unlike most diazonium salts in the dry state, salts **3** are very highly stable.

Key words: stable dry arenediazonium salts, thermal decomposition, azo coupling reactions, *o*-benezenedisulfonimide

It is well known¹ that in the dry state most diazonium salts are quite unstable, being sensitive to physical agents such as heat, light, shock, static electricity etc. that can lead to rapid uncontrollable decomposition and even explosions. This behaviour is particularly dangerous and has certainly had a negative effect on the development of synthetic procedures on a laboratory scale and, even more, on largescale applications. Exceptions to this behaviour are found in most arenediazonium tetrafluoroborates, in some diazonium salts where complex anions are present, *e.g.*, zinc double chlorides and hexafluorophosphates, and in certain arenediazonium sulfonates.

Two brief notes recently described some arenediazonium salts whose counterions are the conjugated bases of bis(trifluoromethylsulfonyl)amine^{2,3} (CF₃SO₂)₂NH (three examples) and the cyclic analog³ $SO_2(CF_2)_3 \tilde{SO}_2NH$ (one example). These salts are remarkably stable in the solid state. Considering that the presence of fluorinated groups is not indispensable, though favourable for the salts' stability, we have thought to advantageously substitute the fluorinated N-anions with the N-anion of o-benzenedisulfonimide (2), to use this as the counterion of arenediazonium cations.⁴ Indeed whereas the synthesis of bis(trifluoromethylsulfonyl)amine and the cyclic analog is very laborious and calls for expensive reagents,⁵ the synthesis of o-benzenedisulfonimide (2) can now be easily realized through simple preparation of o-benzenedisulfonyl chloride, 6,7 the key intermediate to obtain 2.⁸

The preparation of dry arenediazonium salts **3** was easily carried out by diazotization of aromatic amines **1** with *i*-pentyl nitrite in the presence of *o*-benzenedisulfonimide (**2**) in glacial acetic acid or in formic acid at 0-5 °C (Scheme 1). When using acetic acid as the solvent only a few minutes are needed for salts **3** to separate out, and the precipitation can be completed by adding anhydrous Et₂O. When the solvent is formic acid the salts remain in solution; however, in this case the addition of anhydrous Et₂O also leads to their precipitation. In both solvents salts **3** are obtained dry in high purity and excellent yields (Table 1). The crude salt's structure was always verified by



Scheme 1

azo coupling reactions with 2-naphthol to give the corresponding (2-hydroxy-1-naphthyl)aryldiazene **4**. In most cases yields were greater than 90% (Table 1).

With regard to yields of **3**, it is noteworthy that these are significantly higher (usually about 90%) than the yields reported for the diazonium salts containing the fluorinated anions (71-82%).^{2,3} Samples of analytical purity were prepared by crystallization from anhydrous MeCN/Et₂O. Satisfactory elemental analyses and NMR spectra confirmed the structure of the salts. In one case (**3s**) the structure was also supported by an X-ray analysis (Figure, Table 2). Salts **3** are very soluble in water, unlike diazonium salts containing fluorinated anions;^{2,3} furthermore, they are fairly soluble in both polar protic (HCO₂H, MeOH) and aprotic (DMSO, MeCN) solvents. Instead they are essentially insoluble in apolar or slightly polar solvents.

One property that makes salts **3** very interesting is their exceptional stability, a feature that could lead to important synthetic developments. Samples of **3** stored at 0° C for



Figure. X-ray Crystal Structure of Salt 3s

Table 1. Benzenediazonium	o-Benzenedisulfonimides	3a-t and (2-H	vdroxy-1-na	phthyl)ar	vldiazenes 4a-1
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Ar H	Prod-	Yield ^b (%)	dp ^c (°C)	¹ H NMR (CF ₃ CO ₂ D), δ , J (Hz)		Yield	mp ^d (°C)	
	uct ^a				uct	(%)	found	reported
C ₆ H ₅	3 a	98	110	7.40-8.05, 8.05-8.35 (2 m, 7:2, 9H)	4a	94	133	133 ¹³
2-MeC ₆ H ₄	3b	93	105	2.57 (s, 3H), 7.30-8.25 (m, 8H)	4b	86	131	132–133 ¹³
3-MeC ₆ H ₄	3c	92	96	2.32 (s, 3H), 7.30–7.90 (m, 8H)	4 c	85	141	141-142 ¹³
4-MeC ₆ H ₄	3d	91	121	2.37 (s, 3H), 7.40, 8.06, (2d, 1:1, <i>J</i> = 8.5, 4H), 8.65 (m, 4H)	4d	94	134	135-136 ¹³
2-MeOC ₆ H ₄	3e	98	146	3.82 (s, 3H), 6.80–7.20, 7.58, 7.60–8.00 (3m, 1:2:1, 8H)	4 e	94	180	178 ¹⁸
3-MeOC ₆ H ₄	3f	94	90	3.58 (s, 3H), 6.40–7.20, 7.30–7.80 (2 m, 1:3, 8H)	4f	88	140	140 ¹⁸
4-MeOC ₆ H ₄	3g	89	151	3.78 (s, 3H), 6.98, 8.08 (2d, 1:1, <i>J</i> = 8.5, 4H), 7.62 (m, 4H)	4g	99	137	137 ¹⁸
$2-ClC_6H_4$	3h	96	142	7.25-8.02, 8.10-8.40 (2m, 7:1, 8H)	4h	90	163	163 ¹⁹
$3-ClC_6H_4$	3i	96	117	7.30-8.00, 8.00-8.30 (2m, 7:1, 8H)	4i	88	158	158 ¹⁹
$4-ClC_6H_4$	3ј	94	153	7.55, 8.15 (2d, 1:1, <i>J</i> = 8.5, 4H), 7.65 (m, 4H)	4j	92	162	162.5 ¹⁹
3-BrC ₆ H ₄	3k	98	130	7.30–7.90, 7.90–8.50 (2m, 5:3, 8H)	4k	88	172	172 ¹⁹
4-BrC ₆ H ₄	31	95	140	7.58 (m, 4H), 7.68, 8.02 (2d, 1:1, <i>J</i> = 8.5, 4H)	41	89	174	172–173 ¹⁹
$2-NO_2C_6H_4$	3m	98	173	7.58, 7.82-8.80 (2m, 1:1, 8H)	4m	83	211	209-21019
$3-NO_2C_6H_4$	3n	97	157	7.40-8.10, 8.50-8.90, 9.00-9.35 (3m, 5:2:1, 8H)	4n	91	194	193–194 ¹⁹
$4-NO_2C_6H_4$	30	88	143	7.62 (m, 4H), 8.32, 8.58 (2d, 1:1, <i>J</i> = 8.5, 4H)	4o	94	251	251-252 ¹⁹
$4-Me_2NC_6H_4$	3р	99	154	2.92 (s, 6H), 6.53 (d, <i>J</i> = 8.5, 2H), 7.40–7.80 (m, 6H)	4p	84	181	180–182 ²⁰
2,6-Me ₂ C ₆ H ₃	3q	85	108	2.82 (s, 6H), 6.52, 7.62 (2m, 3:4, 7H)	4 q	94	147	147 ²¹
2-MeO- 5-ClC ₆ H ₃	3r	99	151	4.00 (s, 3H), 7.15 (d, <i>J</i> = 8.5, 1H), 7.50–7.85 (m, 5H), 7.92 (s, 1H)	4r	91	204	203 ²²
2,6-Cl ₂ C ₆ H ₃	3s	95	183	7.40–8.10 (m)	4s	92	141	140–141 ²³
1-naphthyl	3t	95	122	7.30-8.10, 8.30-8.72 (2m, 9:2, 11H)	4t	89	230	229-230 ¹³

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^a Satisfactory microanalyses were obtained: C \pm 0.16; H \pm 0.18; N \pm 0.16; S \pm 0.18; Cl \pm 0.16; Br \pm 0.13.

^b Yields obtained by carrying out the reactions in AcOH. Comparable yields were obtained when HCO₂H or HCO₂H/AcOH were used (see experimental).

^c Decomposition point.

^d Crystallization solvent was CHCl₃/PE for compounds **4a–o**, **q–t** and EtOH/PE for compound **4p**.

two months underwent no decomposition; also at room temperature (about 25 °C) for two months, they underwent no changes, the only exceptions being benzenediazonium and o-, m-, and p-toluenediazonium o-benzenedisulfonimides (**3a–d**). Salts **3** have high, well defined and reproducible decomposition points (Table 1) and during decomposition nitrogen is gradually released. Two samples of benzenediazonium o-benzenedisulfonimide (**3a**) were heated, one in the dry state until the decomposition temperature (110 °C), the other, suspended in toluene, to the boiling point of the hydrocarbon (110 °C). Both resulted in two products derived from the loss of nitrogen and phenyl attack at the nitrogen atom of the imide (**5**, Scheme 2) or at an oxygen atom of a sulfonyl group (**6**) which is similar to the behaviour of salts containing fluorinated *N*-anions.^{2,3} Products **5** and **6** are formed in percentages more or less independent of the reaction conditions (**5**:**6** = 66:18 in the dry state and 79:14 in toluene, respectively). In toluene the reaction gave also a small amount (7%) of three isomers derived from phenylation of toluene at the *ortho, meta* and *para* positions (ratio *o:m:p* = 2.2:1.0:1.1). Such a phenylation ratio is consistent with a heterolytic

Table 2. Selected Bond Lengths and Angles for 3s

Bond Length	Å	Bond Angle	(°)
S1-O2	1.439(2)	O2-S1-O1	114.1(1)
S1-N1	1.577(2)	O1-S1-N1	113.7(1)
S2-O4	1.434(2)	O1-S1-C1	107.9(1)
S2-N1	1.586(2)	O4-S2-O3	115.6(2)
Cl1-C8	1.712(3)	O3-S2-N1	113.2(2)
N2-N3	1.088(3)	O3-S2-C6	107.6(2)
S1-O1	1.441(2)	S1-N1-S2	114.6(1)
S1-C1	1.773(3)	C6-C1-S1	110.7(2)
S2-O3	1.440(3)	C1-C6-S2	111.5(2)
S2-C6	1.775(3)	C8-C7-N2	118.3(2)
Cl2-C12	1.701(3)	O2-S1-N1	109.5(1)
N2-C7	1.387(3)	O2-S1-C1	110.6(1)
		N1-S1-C1	100.1(1)
		O4-S2-N1	109.2(2)
		O4-S2-C6	110.8(2)
		N1-S2-C6	99.3(1)
		C2-C1-S1	127.7(2)
		C5-C6-S2	127.7(2)
		N3-N2-C7	178.6(3)
		N2-C7-C12	118.3(3)

process (ratio o:m:p = 2.4:1.0:1.0)⁹ and not a homolytic one (ratio o:m:p = 4.0:1.0:0.7).¹⁰ This clue, together with the gradual and non-violent formation of 5 and 6, drew us to the conclusion that the decomposition of the salts occurs likely via a heterolytic mechanism; decomposition by this route being due to the insufficient electron donor properties of the anion derived from o-benzenedisulfonimide. Thus homolytic reactions, also violent ones, which many arenediazonium salts undergo in the dry state would be avoided for salts 3. In any case the salts fall in line with other empirical rules that give indexes of diazonium salts stability in the dry state: *i*) with only two exceptions (**3c,f**), decomposition points are greater than 100°C;¹¹ ii) the oxygen content is insufficient to convert more than half of the carbon atoms present into CO;^{1d} *iii*) the C/N ratio is >3.^{1d} Still on the subject of stability: it was ascertained that salts 3 can be handled in air and light without decomposition; in our laboratory there was no case of violent decomposition during the preparation, purification and handling of the said salts. Nevertheless it must be borne in mind that there is always a potential danger of explosion for diazonium salts 3 in the dry state, as for all other known diazonium salts in the dry state, even those believed to be quite stable.^{1,11,12}





In conclusion, arenediazonium salts 3, where the counterion of the arenediazonium cations is the anion derived from the now readily accessible o-benzenedisulfonimide (2), show the following characteristic advantages: i) they are easily prepared; ii) they are easily purified; iii) they are normally very highly stable; iv) when salts 3 are reacted in water or organic solvents they give rise, in yields often higher than those obtained using known procedures, to numerous classes of compounds such as azo compounds, phenols, sulfonates, halides, ethers, sulfides etc, as has been shown in previous⁴ and current research; v) at the end of reactions using 3 there is nearly always excellent recovery (usually greater than 90%) of o-benzenedisulfonimide;⁴ vi) most of the salts 3 can be kept in a ready-to-use condition for a long time; *vii*) the results already achieved,⁴ and others related to work in progress, lead us to believe that salts 3 are excellent laboratory reagents, and, furthermore, are valid candidates for technological applications.

¹H and ¹³C NMR spectra were recorded on a Bruker WP 80 SY spectrometer. Mass spectra were recorded on a quadrupole MS Engine HP 5989 B instrument, operating with a direct-inlet system at 70 eV. Petroleum ether refers to the fraction boiling in the range 40–70 °C and is abbreviated as PE. All amines used are available commercially. *o*-Benzenedisulfonimide (2) was prepared according to the literature procedure,⁸ by reaction of *o*-benzenedisulfonyl chloride⁶ and NH₃ gas in EtOH / toluene instead of EtOH / benzene at 0 °C.

CAUTION! All dry diamonium salts are potentially explosive. Therefore they must be carefully stored and handled.

Diazotization of Amines 1: Benzenediazonium *o***-Benzenedisulfonimide (3a); Typical Procedure:**

A solution of o-benzenedisulfonimide (2; 2.63 g, 12 mmol) in glacial AcOH (40 mL) was slowly added, over a period of 10 min, to a stirred solution of aniline (1, Ar = Ph; 0.93 g, 10 mmol) in the same solvent (20 mL), previously cooled to 0-5 °C in an ice bath. *i*-Pentyl nitrite (1.28 g, 11 mmol) was added dropwise at such a rate that the temperature did not exceed 5 °C (about 10 min). A white precipitate of 3a began to separate at once. After the addition was complete, the cooling bath was removed and the mixture was maintained under stirring for a further 5 min. Then anhyd Et₂O was added to complete the precipitation of the diazonium salt that was gathered by filtration on a Büchner funnel and washed several times on the funnel with anhyd Et2O $(6 \times 5-6 \text{ mL})$ to complete the elimination of AcOH. After drying under reduced pressure, the dry title compound 3a was obtained in 98% yield (3.18 g). It was virtually pure (NMR). For analyses, a sample was dissolved in hot anhyd MeCN and then precipitated again with anhyd Et₂O, after cooling; dp (decomposition point) 110°C.

¹H NMR (CF₃COOD): δ = 7.40–8.05 and 8.05–8.35 (2 m, 7 : 2, 9 H). ¹³C NMR (CF₃COOD): δ = 123.35, 123.94, 136.57 (d, CH), 131.77 (2 d, CH overlapped), 140.10 (s, CS), 163.83 (s, CN₂⁺).

Anal. C₁₂H₉N₃O₄S₂ (323.3): calcd C, 44.58; H, 2.81; N, 13.01; S, 19.80; found: C, 44.45; H, 2.76; N, 12.99; S, 19.91.

Salts **3b–s** were prepared in the same way. All the salts were recrystallized as reported above for **3a**. They melted with decomposition, but none exploded. Yields, decomposition points and ¹H NMR data are reported in Table 1.

Diazotization of amines 1a,d,g,j,q,r was also carried out in HCO₂H (20 mL to dissolve 2 and 10 mL to dissolve 1) or in a mixture HCO₂H/AcOH (20 mL of HCO₂H to dissolve 2 and 20 mL of AcOH to dissolve 1). Yields and purity of corresponding salts 3a,d,g,j,q,r were comparable with those obtained when AcOH was used.

Azo Coupling Reactions: (2-Hydroxy-1-naphthyl)phenyldiazene (4a); Typical Procedure:

A solution of 2-naphthol (0.72 g, 5 mmol) in 10% aq NaOH solution (4.4 mL, 11 mmol) was added dropwise over a period of 5 min to a suspension of benzenediazonium o-benzenedisulfonimide (3a; 1.61 g, 5 mmol) in H₂O (20 mL), under vigorous stirring. A red precipitate of 4a began to separate at once. Stirring was continued for 15-20 min until completion of the reaction. Then the mixture was extracted with $CHCl_3$ (3 × 60 mL) and the organic extracts were separated from the aqueous solution and washed with H_2O (2 × 50 mL). After drying (Na₂SO₄) and solvent removal in vacuo, the residue was virtually pure 4a (1.15 g, 93%). The product was furthermore purified by column chromatography (silica gel, CHCl₃); yield unchanged; mp 133°C (CHCl₃/PE) (Lit.¹³ mp 133 °C). Using the same workup as previously described,¹⁴ o-benzenedisulfonimide (2) was recovered from the aqueous solution. This was acidified with concd HCl, concentrated in vacuo until 4–5 mL and then passed through a 15 g column of Dowex 50×8 ion-exchange resin (Fluka), eluting with $\rm H_2O$ (about 15 mL). After removal of H₂O in vacuo, virtually pure (NMR) 2 was recovered in 94% yield (1.03 g); mp 192–194 °C (toluene) (Lit.^{8,14} mp 192–194 °C).

Also diazenes **4b**–**t** were prepared according to the above procedure. In all the cases *o*-benzenedisulfonimide (**2**) was recovered in yields usually greater than 90%. Yields and mp are reported in Table 1.

Thermal Decomposition of Benzenediazonium *o*-Benzenedisulfonimide (3a):

Procedure A: Salt **3a** (1 g) was heated in an oven-dried 10-ml flask equipped with a drying tube, at 110°C (oil bath) for 10 min, until the release of nitrogen ceased and a proof of azo coupling reaction with 2-naphthol was negative. CHCl₃ (5 mL) was added to the solid residue and the mixture was heated under reflux for 5 min. The organic solution was separated by decantation and the insoluble solid substance was washed again with the same solvent (2×2 mL). The crude residue obtained after evaporation of the solvent under reduced pressure was chromatographed on a silica gel column with CHCl₃ as eluent. Compound **6** was obtained in 18% yield (0.16 g). Anhyd MeOH (5 mL) was added to the solid substance which was insoluble in CHCl₃ and the mixture was heated under reflux for 5–10 min. The organic solution was separated by decantation and evaporated under reduced pressure to afford virtually pure (NMR) compound **5** in 66% yield (0.60 g).

Procedure B: A suspension of salt **3a** (1 g) in anhyd toluene (5 mL) was heated at 110 °C as described above. The release of N₂ ceased after 2 h. The organic solution was separated by decantation from the insoluble solid substance which was washed again with toluene (2 × 2 mL). The crude residue obtained after evaporation of the solvent under reduced pressure was chromatographed on a silica gel column with CHCl₃ as eluent. Two fractions were collected. After evaporation under reduced pressure of the first fraction, a solid substance was obtained. GC and GC/MS analyses showed the presence of three products, i.e. *o*-, *m*- and *p*-methyldiphenyl, each with *m*/z 168 (M⁺), in a 2.2:1:1.1 ratio; yield: 7% (0.036 g). Structure of the three isomers was confirmed by comparison with authentic samples (Aldrich). Evaporation of the second fraction afforded compound **6** in 14% yield (0.13 g). The solid substance insoluble in toluene was virtually pure compound **5** (0.72 g, 79%).

Compound **5**: mp 194–195 °C (from MeOH/PE) (Lit.¹⁵ mp 195 °C). ¹H NMR (CF₃COOD): δ = 7.10–7.35 and 7.50–7.80 (2 m, 5:4, 9 H). ¹³C NMR (CD₃OD): δ = 122.85, 124.61, 130.67, 131.68, 134.71 (d, CH), 143.30 (s, CS), 213.73 (s, CN). MS: m/z = 295 (M⁺).

Compound 6: mp 106°C (CHCl₃/PE).

- ¹H NMR (CDCl₃): δ = 7.05–7.70 and 7.95–8.20 (2 m, 5:4, 9 H). ¹³C NMR (CDCl₃): δ = 122.74, 123.58, 128.79, 130.31, 134.35, 136.87 (d, CH), 131.66 (s, CO), 145.12 (s, CS), 148.32 (s, CS). MS: *m*/*z* = 295 (M⁺).
- Anal. $C_{12}H_9NO_4S_2$ (295.3): calcd C, 48.80; H, 3.07; N, 4.74; S, 21.71; found: C, 48.72; H, 3.04; N, 4.69; S, 21.65.

X-ray Analysis of Compound 3s:

Crystals of 3s (C12H7Cl2N3O4S2), grown by slow evaporation from MeCN, are monoclinic: a = 7.360(1), b = 16.391(2), c = 13.173(2) Å, $b=99.6(1)^{\circ},\,V=1566.9$ Å $^{3},\,D_{calc}=1.663$ g/cm $^{3},\,Z=4,\,space$ group P21/c. The unit-cell parameters and intensities of 3791 independent reflections were measured on a Philips PW110 four-circle diffractometer, using graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å), $\theta - 2\theta$ scan mode up to $\theta_{max} = 28^\circ$. The structure was solved by direct methods of SHELXS-86 program.¹⁶ Refinement was carried out by full-matrix least-squares on F^{2} , using the full dataset, with anisotropic displacement parameters for all non-hydrogen atoms, by application of the SHELXL-93 program.¹⁷ Hydrogen atoms were included at calculated positions with idealized geometry, and during the refinement they were allowed to ride on their carrying atom, with Uiso set equal to 1.2 times the U_{eq} of the atom to which they are bonded. Refinement converged to $R_1 = 0.039$ [on F, for 2407 reflections with F_o $\geq 4(\sigma)F_0$ and wR₂ = 0.125 (on F²) for all data. The data / restraints / parameters ratio was 3791 / 0 / 208. Goodness of fit = 0.970. Maximum shift / e.s.d.s. 0.001. Maximum and minimum $\Delta \rho$ in the final difference Fourier map: +0.45 and -0.32 e/Å³. Selected bond lenghts and bond angles are listed in Table 2. Complete lists of fractional atomic coordinates, bond distances, bond angles, and anisotropic displacement parameters have been deposited and are available at the Cambridge Crystallographic Data Centre.

This work was supported by the National Research Council of Italy (CNR), Legge 95/95 and by Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST).

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