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Crystallographic characterisation of arenesulfonyl azides. Structural and kinetic effects induced by *ortho*- and *para*-substituents

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The molecular structures of six arenesulfonyl azides, $ArSO_2N_3$ (Ar = 4-nitrophenyl, 4-acetylphenyl, 4-methoxyphenyl, 2-nitrophenyl, 2,4,6-triisopropylphenyl or ferrocenyl group), have been characterised by X-ray diffraction studies. The N–N bond lengths are influenced only to a negligible extent by the nature of *para*-substituents. In contrast, the C–S and S–N distances are sensitive to the electron-withdrawing power of *para*-substituents and undergo opposing changes. These bond lengths as well as the $\nu_{as}(N_3)$ frequencies of the 4-substituted azides show linear dependencies as a function of Hammett's σ constants, which agree well with earlier results on the relative reactivities of arenesulfonyl azides toward $[Pd_2Cl_2(dppm)_2]$. The unusual structural properties of *o*-nitrobenzenesulfonyl azide are attributed to dipole–dipole interactions of the nitro group with the sulfonyl and the azide moieties. Although electronic effects due to *para*-substituents govern the magnitude of the second-order rate constants, the reactivity of *o*-nitrobenzenesulfonyl azide seems to be determined by steric interactions.

Introduction

Organic azides can interact with metal complexes in many different ways. As witnessed by numerous reports on this subject, cleavage of the azide moiety with concomitant production of imido (nitrene) complexes and dinitrogen undoubtedly represents the major route of transformation.[1] The integrity of the NNN linkage is preserved, however, when, simultaneously with the formation of metal–nitrogen bond(s), N–H, N–C, N–N or N–P bonds are also created.[2] Earlier, pure azide complexes, in which the α and γ nitrogens are coordinated exclusively to metal centres, were implicated only in mechanistic considerations.[3] Recently, however, several pieces of experimental evidence[4] have emerged, demonstrating that organic azides can actually be stabilized in the coordination sphere of a metal ion without involving anything other than metal–nitrogen bonding interactions. Studies on these isolated complexes have revealed not only the structural diversity of the azide ligands but have also shed light on the mechanistic details of their conversion into coordinated nitrene species.

In the course of our search for a viable route to arenesulfonylimido complexes of palladium, we have observed that the interaction of palladium dimer **1** with arenesulfonyl azides **2** results in the formation of dimeric A-frame imido adducts $[Pd_2Cl_2(dppm)_2(\mu\text{-}NSO_2Ar)]$ (**3**) (dppm is bis(diphenylphosphino)methane).[5]

$$\underset{\mathbf{1}}{[Pd_2Cl_2(dppm)_2]} + \underset{\mathbf{2}}{ArSO_2N_3} \xrightarrow{-N_2} \underset{\mathbf{3}}{[Pd_2Cl_2(dppm)_2(\mu\text{-}NSO_2Ar)]} \quad (1)$$

Although nitrene complexes **3** could be isolated as sole products with most azides studied, a minor constituent in varying amounts (<15%) was also detected when 2-nitrobenzenesulfonyl azide was used as a reagent. Efforts to identify this by-product have led to the spectroscopic and crystallographic characterisation of complexes bearing arenesulfonyl azides as ligands, such as $[Pd_2Cl_2(dppm)_2(\mu\text{-}N_3SO_2C_6H_4NO_2)]$[5] and $[Pd_2Cl_2(dppm)_2(\mu\text{-}N_3SO_2C_6H_2\{i\text{Pr}\}_3)]$.[6]

From our kinetic studies on reaction (1), we have concluded that the formation of the imido adduct takes place *via* an associative bimolecular mechanism in which the transition state requires only a small extent of bond-breaking (small $\Delta H^\ddagger$) but extensive ordering of the reactants and solvent molecules (large negative $\Delta S^\ddagger$).[7] It has also been demonstrated that the second-order rate constants of the 4-substituted arenesulfonyl azides obey the Hammett equation.

In order to understand the physical background of the kinetic behaviour of the azides investigated, we compared some of their structural data. Surprisingly, with the only exception of an early IR study[8] on 4-substituted arenesulfonyl azides, we could not find any systematic structural investigation of these substances.

In this communication we describe the crystal and molecular structures of six arenesulfonyl azides as determined by single crystal X-ray diffraction and analyse the relationship of structural parameters like bond lengths and IR frequencies from the point of view of their reactivities toward dimer **1**. The unusually high $\nu_{as}(N_3)$ frequency of 2-nitrobenzenesulfonyl azide and its anomalous reaction rate with **1** will also be discussed on the basis of X-ray structural data.

Results and discussion

Systematic structural characterisation of organic azides is justified by the long-standing interest toward their application in organic and organometallic reactions.[9] To our knowledge, the only attempt to obtain crystallographic data for a sulfonyl azide was made on the ferrocene derivative $FcSO_2N_3$ but this work does not seem to be completed.[10] We hope that a reinvestigation of this compound may help us to understand the fine structural details not disclosed in the earlier study. In this communication, the aryl group represents a phenyl ring substituted in the *para*-position with a nitro (**2a**), acetyl (**2b**) or methoxy (**2c**) group or denotes 2-nitrophenyl (**2d**), 2,4,6-

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Table 1 Crystallographic data and data collection parameters

Compound	**2a**	**2b**	**2c**	**2d**	**2e**	**2f**
Aryl group	4-$NO_2C_6H_4$	4-[$CH_3C(O)$]C_6H_4	4-(CH_3O)C_6H_4	2-$NO_2C_6H_4$	2,4,6-(iPr)$_3C_6H_2$	Fc
Empirical formula	$C_6H_4N_4O_4S$	$C_8H_7N_3O_3S$	$C_7H_7N_3O_3S$	$C_6H_4N_4O_4S$	$C_{15}H_{23}N_3O_2S$	$C_{10}H_9FeN_3O_2S$
Formula weight	228.19	225.23	213.22	228.19	309.42	291.11
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$Pna2_1$	$P\bar{1}$	$P2_1/c$	$P1/c$	$P2_1/n$	$P2_1/n$
Unit cell dimensions						
a/Å	16.318(1)	7.083(1)	5.174(1)	7.908(1)	5.997(1)	5.984(1)
b/Å	10.782(1)	7.309(1)	10.727(1)	14.572(1)	21.456(2)	35.194(1)
c/Å	10.295(1)	10.280(1)	16.762(1)	8.238(1)	13.579(1)	10.795(1)
α/°		97.73(1)				
β/°		108.70(1)	94.22(1)	106.59(1)	95.88(1)	92.29(1)
γ/°		100.06(1)				
V/Å^3	1811.3(3)	485.9(1)	927.8(2)	909.8(2)	1738.0(4)	2271.6(4)
Z	8	2	4	4	4	8
Absorption coefficient, μ/mm^{-1}	0.359	0.323	0.333	0.357	0.194	1.503
Reflections collected	7933	3507	4027	4292	4070	5175
Independent reflections	7933 [R(int) = 0.0040]	3507 [R(int) = 0.0095]	4027 [R(int) = 0.0054]	3940 [R(int) = 0.0094]	4070 [R(int) = 0.0193]	5175 [R(int) = 0.0148]
Reflections $I > 2\sigma(I)$	5584	2512	3030	2222	2121	3490
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0338$, $wR2 = 0.0845$	$R1 = 0.0397$, $wR2 = 0.1102$	$R1 = 0.0398$, $wR2 = 0.1220$	$R1 = 0.0354$, $wR2 = 0.0882$	$R1 = 0.0494$, $wR2 = 0.1228$	$R1 = 0.0335$, $wR2 = 0.0881$
R indices (all data)	$R1 = 0.0579$, $wR2 = 0.0911$	$R1 = 0.0565$, $wR2 = 0.1192$	$R1 = 0.0533$, $wR2 = 0.1284$	$R1 = 0.0830$, $wR2 = 0.0967$	$R1 = 0.1074$, $wR2 = 0.1385$	$R1 = 0.0678$, $wR2 = 0.0967$

Table 2 Selected bond lengths (Å) and angles (°) of arenesulfonyl azides **2a**–**2f**

	4-$NO_2C_6H_4$		4-[$CH_3C(O)$]C_6H_4	4-(CH_3O)C_6H_4	2-$NO_2C_6H_4$	2,4,6-(iPr)$_3C_6H_2$	Fc	
Aryl group	**2a/1**	**2a/2**	**2b**	**2c**	**2d**	**2e**	**2f/l**	**2f/2**
N(1)–N(2)	1.256(2)	1.260(3)	1.251(2)	1.247(2)	1.199(2)	1.213(3)	1.218(3)	1.236(4)
N(2)–N(3)	1.101(2)	1.114(3)	1.101(2)	1.109(2)	1.062(2)	1.19(2)	1.128(4)	1.121(4)
S(1)–N(1)	1.678(1)	1.694(2)	1.686(1)	1.707(1)	1.686(1)	1.727(2)	1.724(2)	1.713(3)
S(1)–C(1)	1.760(1)	1.764(1)	1.753(1)	1.737(1)	1.769(1)	1.773(2)	1.712(2)	1.718(3)
S(1)–O(1)	1.429(1)	1.425(1)	1.427(1)	1.424(1)	1.442(1)	1.408(2)	1.416(2)	1.419(2)
S(1)–O(2)	1.423(1)	1.420(1)	1.424(1)	1.424(1)	1.393(1)	1.410(2)	1.424(2)	1.415(2)
N(1)–N(2)–N(3)	174.3(2)	173.5(2)	172.9(2)	174.2(1)	172.6(1)	168(1)	173.7(3)	173.1(4)
S(1)–N(1)–N(2)	112.9(1)	111.6(1)	113.7(1)	112.5(1)	112.2(1)	113.2(2)	113.0(2)	111.4(2)
C(1)–S(1)–N(1)	104.0(1)	103.3(1)	103.4(1)	103.9(1)	101.0(1)	102.6(1)	102.7(1)	102.7(1)
O(1)–S(1)–O(2)	121.5(1)	121.2(1)	120.9(1)	120.7(1)	117.7(1)	119.6(1)	121.1(1)	120.7(1)
Δ[N(1)–S(1)–O]	6.5	5.5	6.5	5.3	12.8	2.9	5.3	4.5

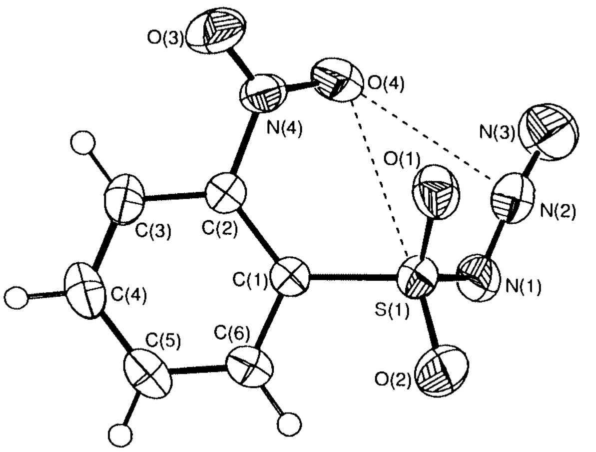

Fig. 1 Molecular diagram of **2d** with the numbering of atoms. Atomic displacement parameters represent 40% probabilities.

triisopropylphenyl (**2e**) or ferrocenyl (Fc) (**2f**) moieties. Crystal data and data collection parameters are summarised in Table 1.† Selected bond lengths and angles are collected in Table 2.

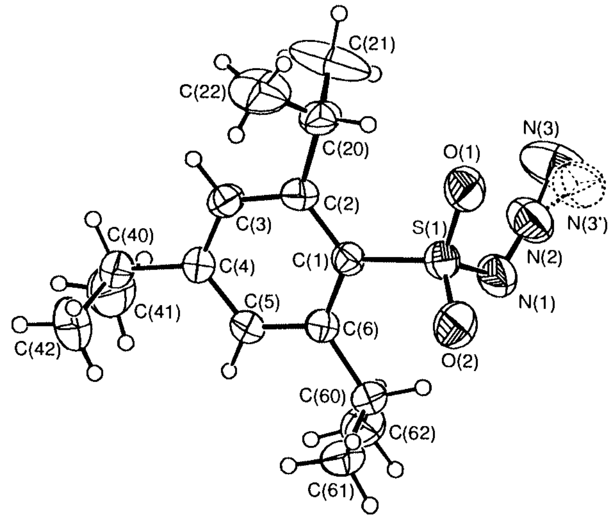

Fig. 2 Molecular diagram of **2e** with the numbering of atoms. Atomic displacement parameters represent 40% probabilities.

The molecular structures of **2d**, **2e** and **2f** are shown in Figs. 1–3.

It is noteworthy that most of the azides showed excellent stability during data collection. A *ca.* 40% loss of intensity was

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† CCDC reference number 188/255. See http://www.rsc.org/suppdata/p2/b0/b004337k/ for crystallographic files in .cif format.

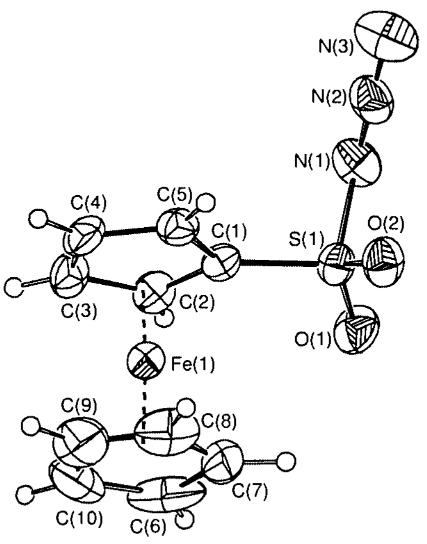
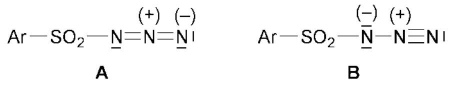


Fig. 3 Molecular diagram of **2f** with the numbering of atoms. Atomic displacement parameters represent 40% probabilities.

experienced, however, in the case of **2f** but this did not hinder structure elucidation. Unfortunately, our attempts to grow crystals of sulfonyl azides of low melting points (<40 °C) were not successful.

In the azide ion, the nitrogen–nitrogen bonds are identical (d_{NN} = 1.166 Å) but in covalently bound azides the N_3 group is asymmetric and the bond length between the α and β nitrogen atoms is considerably longer than that between the β and γ nitrogens. The distribution of the valence electrons is generally illustrated by two canonical structures (**A** and **B**) which, if



$$\text{Ar}-\text{SO}_2-\overset{(+)}{\text{N}}=\overset{(-)}{\text{N}}=\text{N} \qquad \text{Ar}-\text{SO}_2-\overset{(-)}{\text{N}}-\overset{(+)}{\text{N}}\equiv\text{N}$$

A **B**

they have equal contributions, result in bond orders of 1.5 and 2.5, respectively.[11] The N(1)–N(2) distances of **2a**–**2c** are much shorter than the typical N–N single bond (hydrazine, 1.45 Å)[12] and are close to that found in (*E*)-azobenzene [1.247(2) Å].[13] The N(2)–N(3) bond lengths are not very different from that in dinitrogen (1.098 Å). Although the experimentally found bond lengths would suggest bond orders close to 2 and 3 for the two N–N interactions, this assumption would break the octet rule for the central nitrogen atom. Consequently, the effective bond orders are certainly smaller for both bonds. The considerable difference between the N(1)–N(2) and N(2)–N(3) bond lengths is indicative of the readiness to form nitrene species both thermally and photochemically *via* elimination of N_2 as has been demonstrated by detailed investigations on this topic.[14]

As is shown in Table 2, the N(1)–N(2) and N(2)–N(3) distances undergo only negligible changes on going from the 4-nitro to the 4-methoxy derivative but the S(1)–N(1) bonds are noticeably affected by the electronic nature of the substituent on the phenyl ring. In **2a**, the mean S–N bond length of the two crystallographically independent molecules is 1.686(1) Å, which increases to 1.707(1) Å in **2c**. A reverse trend is observed for the C(1)–S(1) distance. The strongly electron-withdrawing nitro group results in a relatively long C–S bond [d_{av} = 1.762(1) Å] that shrinks to 1.737(1) Å in **2c** which has an electron-donating substituent.

A search of the Cambridge Structural Database (CSD)[15] (October 1999 release) revealed a median of 1.288 Å for N(1)–N(2) and 1.127 Å for N(2)–N(3). A subgroup of aliphatic compounds, constituting the majority of organoazides found, has almost identical statistical bond lengths. Another, though much less numerous group of azides in which the N_3 unit is conjugated to C=C, C=N or C=O double bonds has medians (1.249 and 1.116 Å) approaching the respective geometric data for **2a**–**2c**.

The structural modifications induced by the *para*-substituents can be summarised as follows. In the case of arenesulfonyl azides, the highly electrophilic sulfonyl group interacts with both the aryl and azide moieties. When Ar is 4-nitrophenyl (**2a**), the aryl group has poor electron-donating properties and a relatively long C–S bond is formed. The electron deficiency of the SO_2 unit is then satisfied mostly by the azide unit, leading thereby to a relatively short S–N distance. An opposite trend is observed when the benzene ring carries a methoxy functionality (+*R* effect). In this case, the Ar group is a good electron donor and the C–S bond becomes comparatively short. This results in a less extensive interaction of the azide moiety with the sulfonyl group, as reflected by the long S–N distance in **2c**.

An inspection of the respective data of ferrocenesulfonyl azide supports the above considerations. Ferrocene is known to have high electron density on the cyclopentadienyl ring, which results in enhanced rates in electrophilic substitutions compared to the same type of reactions with benzene.[16] The remarkably short C–S bond in **2f** can be attributed to the excellent electron-donating ability of the ferrocenyl group. As a consequence of the strong interaction of the sulfonyl and ferrocenyl units, the SO_2 group exerts an attenuated polarization on the azide moiety, which leads to an outstandingly long S–N distance and more uniform N–N bonds as well.

Due to the disorder of N(3), a discussion of the structural data of **2e** requires caution. As alkyl groups exert an activating effect in electrophilic reactions, the isopropyl groups enhance the electron-donating ability of the aryl ring, and the S(1)–N(1) bond length in **2e** is in line with expectations. The surprisingly long C(1)–S(1) bond, however, seems to contravene the trend observed, because a carbon–sulfur bond length comparable to that in **2c** could be expected for **2e**. The elongation of this bond can certainly be ascribed to steric hindrance emerging between the bulky sulfonyl group and the large *o*-isopropyl substituents. To minimise steric interactions, the methyl groups are pointing away from the SO_2 unit, which is still closer to the methine hydrogen atoms $\{d[\text{O}(1)\cdots\text{H}(20)] = 2.025$ Å, $d[\text{O}(2)\cdots\text{H}(60)] = 2.367$ Å$\}$ than the O(1)···H(6) and O(2)···H(2) distances in **2a**–**2c** (2.55–2.73 Å).

The crystallographic data presented, especially those for **2a**–**2c**, provide evidence about structural changes occurring in the vicinity of the sulfonyl group upon varying the substituents on the aryl ring. It remains obscure, however, if the electronic properties of the *para*-substituents influence the bond lengths (and bond orders) within the N_3 moiety. The insensitivity of the N–N bonds toward substitution on the aryl group can easily be explained by noting that the bond orders of the C(1)–S(1) and S(1)–N(1) bonds are around 1, while those within the N_3 fragment are *ca.* 1.5 and 2.5 for N(1)–N(2) and N(2)–N(3), respectively. Therefore, redistribution of valence electrons induced by the *para*-substituents brings about detectable changes in bonds described as having bond orders of *ca.* 1, but bonding interactions of multiple character are influenced only to an extent that falls in the range of standard deviations of the crystallographic data. The problem resembles the case of metal carbonyl complexes, where metal to CO back-donation can conveniently be detected *via* changes in the metal–carbon bond lengths. Variations of the C–O distances in the carbonyl ligand, having generally a bond order of >2.5 are, however, at the sensitivity limit of crystallography.[17] Fortunately, IR spectroscopy can reveal these small structural changes.

The asymmetric stretching frequencies, $\nu_{as}(N_3)$, for the arenesulfonyl azides studied are collected in Table 3. The spectroscopic data clearly demonstrate that the *para*-substituents on the phenyl ring influence not only the C(1)–S(1) and S(1)–N(1) bonds but also the N–N bond lengths. Electron-withdrawing substituents, which lead to relatively short S(1)–N(1) bond

Table 3 IR spectroscopic data and second-order rate constants of arenesulfonyl azides

Aryl group	ν/cm^{-1}	k^a/M^{-1} s^{-1}
4-$NO_2C_6H_4$	2131.2	0.406
4-$CH_3C(O)C_6H_4$	2128.1	0.104
4-FC_6H_4	2127.3	0.044
C_6H_5	2126.9	0.0258
4-$CH_3C_6H_4$	2125.0	0.0161
4-$CH_3OC_6H_4$	2123.8	0.0140
2-$NO_2C_6H_4$	2147.7	0.058
2,4,6-(*i*Pr)$_3C_6H_2$	2123.7	
Fc	2123.7	

^{a} Measured at 15 °C (kinetic data are taken from ref. 7).

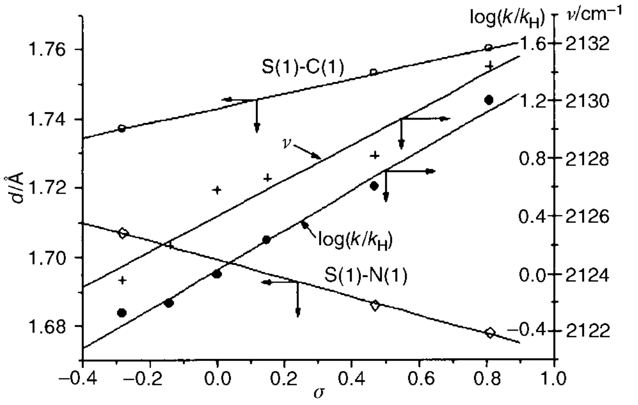


Fig. 4 Dependence of the C(1)–S(1) and N(1)–S(1) bond lengths, the $\nu_{as}(N_3)$ frequencies and the second-order rate constants (k) on Hammett's σ constants.

lengths, increase the $\nu_{as}(N_3)$ frequency, while electron-rich aryl groups bring about an opposite trend. Although the structural effects are undoubtedly small and $\Delta\nu$ for the *para*-nitro and *para*-methoxy derivatives amounts to only 7.4 cm^{-1}, changes induced by these substituents in the distribution of valence electrons do strongly affect the reactivity of arenesulfonyl azides toward the palladium complex [$Pd_2Cl_2(dppm)_2$]. This is convincingly shown by the ratio of second-order rate constants k(4-NO_2)/k(4-MeO) of *ca.* 30 (at 15 °C) for the fastest and slowest reactions.

The S(1)–N(1) and S(1)–C(1) bond lengths as well as the $\nu_{as}(N_3)$ frequencies show a linear dependence on Hammett's σ constants (see Fig. 4). The identical trends in the IR and kinetic data are noteworthy and indicate that changes in the structural parameters and in the reactivities have a common origin. The correlation of the IR data with the Hammett parameters has been observed for an almost identical series of sulfonyl azides.[8]

Spectroscopic and kinetic investigations with 2-nitrobenzenesulfonyl azide, **2d**, seem to contradict all the conclusions reached in relation to the *para*-substituted reagents. The $\nu_{as}(N_3)$ band of the most reactive azide (**2a**) shows up at 2131.2 cm^{-1}, while the same vibration in **2d** appears at 2147.7 cm^{-1}. This remarkably high value is not accompanied, however, by an increased reactivity of **2d** toward **1**, as could be expected from a simple extrapolation of the spectroscopic and kinetic data. Instead, as demonstrated by our studies, k(2-NO_2) is about 7 times smaller than k(4-NO_2). Obviously, we need an explanation for the irregular structural and kinetic behaviour of **2d**.

Structural data for 2-nitrobenzenesulfonyl azide show that **2d** has extraordinary properties not only in solution but also in the solid state. The most striking features are (*i*) the unusually short N–N bond lengths which are markedly smaller than the respective distances in the *para*-substituted azides, and (*ii*) the inequivalence of S(1)–O(1) and S(1)–O(2) bonds deviating by *ca.* 0.05 Å. In contrast the S–O bond lengths are practically equal in all the other sulfonyl azides described in this study.

The crystallographic data also reveal other unexpected structural details, *e.g.* the inequivalence of the N–O bonds and the short N(4)–C(2) bond length compared to that of N(4)–C(4) in **2a**. Moreover, the intramolecular non-bonded interactions O(4)···S(1) (3.07 Å) and O(4)···N(2) (2.84 Å) are smaller than the sums of the van der Waals radii.

Obviously, inductive and mesomeric effects cannot be responsible for these structural pecularities. For a nitro group, free of steric interactions, a coplanar arrangement with an aryl ring represents the energetically most favourable position. Due to the bulkiness of both substituents in **2d**, this is not feasible as shown by the dihedral angle of the phenyl ring with the O(3),N(4),O(4) plane (35.1°). The loss of coplanarity is expected to result in a less extensive interaction of the nitro group with the aromatic system, which, in turn, could lead to a *decrease* in $\nu_{as}(N_3)$ in the case of **2d**. Twisting of the nitro group around the C(2)–N(4) bond opens, however, a route for interaction not available to a nitro group in the *para*-position. The O(4) atom carrying partial negative charge seems to be involved in dipole–dipole interactions with the S(1) and N(2) atoms, both representing the positive ends of their own dipoles. This structural feature of **2d** seems to be related to earlier observations on *o*-nitrobenzenesulfenic acid and -sulfinic acid derivatives[18] and is being further examined in this laboratory. Weak attractions such as S(1)···O(4) and N(2)···O(4) are generally termed as through-space non-bonded interactions, which, if they emerge due to advantageous steric arrangements, generally cause a much more powerful redistribution of the valence electrons than through-bond polarisations.[19] The pronounced shortening of the N–N bonds, that is also reflected by the outstandingly high frequency of the $\nu_{as}(N_3)$ band, is thus ascribed to dipole–dipole interactions of the participating sulfonyl, nitro and azide moieties. In the case of **2d**, these combined effects make the azide group more electrophilic than in any other sulfonyl azides studied here. The coincidence of solution (IR) and solid phase structural data allows us to conclude that the arrangement of the interacting groups is energetically favourable and the interaction observed in the solid state does not vanish in solution. Thus, the crystallographic data show that it is the interaction of the nitro group with the sulfonyl and the azide units that turns **2d** into a rather exceptional example.

Significantly, the interacting O(4) atom forms a shorter bond with the N(4) atom than does O(3). We tentatively attribute this observation to the asymmetric polarization of the nitro group by its neighbours. The S(1) and N(2) atoms presumably change the spatial distribution of the non-bonding electrons on O(4), thereby reducing the repulsive interactions associated with them, but leave the attracting forces between O(4) and N(4) undisturbed.

Although we ascribe most of the structural peculiarities of **2d** to non-bonded interactions of the nitro group with the sulfonyl and azide moieties, its decreased reactivity requires further explanation. The formation of the activated complex of reaction (1) is accompanied by extensive ordering of the reagents and/or solvent molecules as indicated by the large negative $\Delta S^\ddagger$ values. According to our mechanistic considerations, the formation of nitrene adduct is preceded by the generation of an azide complex in which both the α and the γ nitrogens are coordinated.[5,7] It seems plausible to suppose that a substituent in the *ortho*-position brings about additional disadvantageous interactions with the phenyl groups of the dppm ligands and decreases the rate of the reaction which leads to the nitrene complex.

As for the role of the 2-nitro substituent, we can conclude that it exerts two opposite effects on the reactivity. By interacting with the sulfonyl and azide groups, it makes the azide moiety more electrophilic and, as judged from the structural data, an exceptionally high reactivity can be expected. On the other hand, the steric hindrance at the *ortho*-position suppresses the potentially high reactivity and the reaction rate becomes governed by steric rather than electronic factors. The importance of steric effects in the interaction of arenesulfonyl azides with **1** has been documented in the case of 2,4,6-triisopropylbenzenesulfonyl azide.[6]

Conclusions

X-Ray diffraction and IR spectroscopic studies on arenesulfonyl azides were carried out to reveal the structural effects induced in the -SO_2N_3 moiety by aryl groups with various electronic properties. The systematic modifications in structural parameters like bond lengths and $\nu_{as}(N_3)$ frequencies suggest that the structural changes brought about by substituents of varying electron-donating ability can be explained in terms of the varying contribution of canonical structures **A** and **B**. Electron-rich aryl moieties seem to increase the role of form **A**, while aryl groups having electron-withdrawing substituents increase the inequivalence of the N–N bonds and support form **B**. This conclusion is in line with the observed trend of the second-order rate constants, because sulfonyl azides receiving a larger contribution of **A**, carrying a negative charge close to the reaction centre, show lower reactivities toward a nucleophilic metal–metal bond of a palladium dimer.

The structural peculiarities of 2-nitrobenzenesulfonyl azide have been attributed to dipole–dipole interactions of the nitro group with the sulfonyl and azide units. The moderate rate constant of **2d** compared with that predictable from its structural data was attributed to steric hindrance. It seems reasonable to suppose that the potentially high reactivity of **2d** as an electrophile will be observed in sterically less congested reactions.

Experimental

Arenesulfonyl azides[20] and $[Pd_2Cl_2(dppm)_2]$[21] were synthesised by established procedures. The IR spectra were recorded at ambient temperature on 0.02–0.05 M solutions of azides in CCl_4 using a Nicolet 205 FTIR spectrometer.

X-Ray diffraction studies: intensity data were collected on an Enraf-Nonius CAD4 diffractometer (graphite monochromator, Mo–Kα radiation, $\lambda = 0.71073$ Å) at room temperature. Empirical psi-scan absorption corrections[22] were applied in all cases. The structures were solved by direct methods[23] and were refined by anisotropic full-matrix least-squares[24] on F^2. Hydrogen atomic positions were generated from assumed geometries. Neutral atomic scattering factors and anomalous scattering factors are taken from ref. 25. The PLATON program[26] was used for molecular graphics.

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