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CRYSTALLOGRAPHIC STUDIES OF INTRA- AND INTER-MOLECULAR INTERACTIONS.

PART VI. CRYSTAL AND MOLECULAR STRUCTURE OF *N*, *N*′-DIMETHYL-*N*′-PHENYLSULPHONYLFORMAMIDINE. EQUALIZATION OF CN BOND LENGTHS IN THE AMIDINE FRAGMENT AS A RESULT OF SUBSTITUENT EFFECTS DUE TO PUSH–PULL

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The crystal and molecular structure of *N*,*N*-dimethyl-*N*′-phenylsulphonylformamidine is solved by direct methods and refined to $R = 0{\cdot}041$ for 935 reflections. Equalization of CN bond lengths in the amidine fragment is discussed in terms of a push–pull effect operating between the *N*,*N*-dimethyl and SO_2Ph groups. A significant role of the substituent at the functional carbon on the degree of π-electron delocalization on the NCN fragment is interpreted by use of the HOSE model

INTRODUCTION

The amidine skeleton in general is built up of one single and one double CN bond.[1] This rule is broken, however, in the case of amidines which exist in the crystal lattice as dimers or for amidinium salts.[2] In these systems, considerable equalization of the longer CN(l) and the shorter CN(s) bond lengths is observed. Push–pull interactions between substituents in π-electron systems are known to stabilize such systems,[3,4] and hence in principle should lead (at least partially) to equalization of the lengths of bonds differing in their chemical nature.[5] Push–pull molecules are built up by attaching an electron-donating substituent D and an electron-accepting substituent A to two sides of a c jugated π-system. The contribution of canonical str tures $D^+{=}CHCH{-}A^-$ or D^+PhA^- to the electr distribution has recently been extensively studied.[6] T amidine N—C=N skeleton provides a type of str tural unit which contains both the donating gro (R_1R_2N—) and the transmitting unit (—C=N—).

We report here an x-ray diffraction study *N*, *N*-dimethyl-*N*′-phenylsulphonylformamidine, push–pull amidine in which the pulling group, SO_2 is one of the strongest electron-accepting substituen The substituent constants are as follows: $\alpha_F = 0{\cdot}63$ (that for NO_2, $\sigma_F = 0{\cdot}65$),[7] $\sigma_{\bar{R}}$ (SO_2Ph) $= 0{\cdot}95$ or 1· depending on the source[8] [cf. $\sigma_p(NO_2) = 1{\cdot}27$].[8] P viously reported structures of push–pull amidines re to the weaker pulling group *p*-$PhNO_2$.[9] The aim of t work was to study how strongly push–pull interacti may affect the classical geometry of the N—C= group.

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† Two supplementary Tables are available from the author on request.

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EXPERIMENTAL

N^2-Benzenesulphonyl-N^1, N^1-dimethylformamidine was synthesized as described previously[10] from dimethylformamidine dimethylacetate and benzenesulphonamide and recrystallized from methanol. Crystals of N^2-benzenosulphonyl-N^1, N^1-dimethylformamidine were crystallized from ethanol.

An Enraf-Nonius CAD-4 diffractometer was used with graphite monochromatized Mo Kα radiation. The crystal size was $0{\cdot}3 \times 0{\cdot}2 \times 0{\cdot}2$ mm. Unit cell parameters were obtained by least-squares fitting of the setting of 25 reflections in the ϑ range $10^\circ \leqslant \vartheta \leqslant 27^\circ$. The intensities of 1322 reflections were measured [$\sin \vartheta/\lambda \leqslant 0{\cdot}64$, $h \leqslant 7$, $k \leqslant 15$, $l \leqslant 17$]. The data were corrected for Lorentz and polarization effects but no absorption correction was applied. Of 1301 unique reflections, 935 with $F_0 \geqslant 3\sigma(F_0)$ were used in the calculations.

The structure was solved by direct methods, block-matrix least-squares refinement minimizing $\Sigma w(|F_0| - |F_0|)^2$, weights $w = 1/[\sigma^2(F_0) + 0{\cdot}001(F_0)^2]$. Heavy atoms were refined anisotropically and all H atoms were obtained from a difference map and refined with an isotropic temperature factor, giving 176 parameters. Final $R = 0{\cdot}0407$, $wR = 0{\cdot}0396$ for 935 reflections, the final difference Fourier map showed $\Delta\rho_{\max} = 0{\cdot}21$ and $\Delta\rho_{\min} = -0{\cdot}36$ e Å^{-3}, maximum Δ/σ in the final cycle $= 0{\cdot}258$, average $\Delta/\sigma = 0{\cdot}06$. The computer programs SHELXS[11] SHELX-76[12] were used. Molecular illustrations were drawn using PLUTO.[13] Atomic scattering factors were taken from the *International Tables for X-Ray Crystallography.*[14]

RESULTS AND DISCUSSION

Crystal data are given in Table 1, atomic parameters in Table 2, bond lengths and bond angles in Table 3 and a view of the molecule with the atom numbering scheme in Figure 1. The amidine skeleton and the S- atom form a plane with insignificant deviations from it (the greatest deviation for C is 2·1 estimated standard deviations (esd)). This plane forms an angle with the plane of the benzene ring of 103·9(1)°. Hence these two π-electron systems should be discussed separately.

Table 1. Crystal data

$C_9H_{12}N_2O_2S$	$D_x = 1{\cdot}39$ g cm^{-3}
$M_r = 212{\cdot}27$	λ(Mo Kα) $= 0{\cdot}70930$ Å
Orthorhombic	μ(Mo Kα) $= 2{\cdot}46$ cm^{-1}
$P2_12_12_1$	$F(000) = 448$
$a = 5{\cdot}911(2)$ Å	$T = 295$ K
$b = 12{\cdot}476(2)$ Å	$R = 0{\cdot}0407$
$c = 13{\cdot}776(2)$ Å	$wR = 0{\cdot}0396$
$V = 1015{\cdot}9$ Å^3	935 reflections
$Z = 4$	

Table 2. Atomic fractional coordinates ($\times 10^4$) (esd values in parentheses) with thermal parameters $B_{eq} = 8\pi^2 D_u^{1/3}(\sin\alpha^2 \sin\beta^2 \sin\gamma^2)$, where D_u is the determinant of the U_{ij} matrix

Atom	X/A	Y/B	Z/C	B_{eq}
C(1)	1512(7)	4286(3)	5212(2)	2·7
C(2)	3590(7)	4401(3)	4761(3)	3·4
C(3)	3990(8)	3847(3)	3907(3)	4·1
C(4)	2362(9)	3187(3)	3527(3)	4·1
C(5)	296(8)	3083(3)	3974(3)	4·1
C(6)	− 147(7)	3629(3)	4826(3)	3·5
C(7)	3680(7)	4242(3)	7538(2)	2·8
C(8)	2984(8)	2753(4)	8632(4)	4·6
C(9)	6653(7)	3754(3)	8665(3)	4·1
N(1)	1679(6)	4140(2)	7145(2)	3·3
N(2)	4411(5)	3606(2)	8231(2)	3·2
O(1)	2349(5)	5928(2)	6305(2)	4·2
O(2)	− 1460(5)	5122(3)	6382(2)	4·5
S	967(2)	4980(1)	6310(1)	3·3

Table 3. Bond lengths and bond angles with esd values in parentheses

Bond	Length (Å)	Bond	Angle (°)
C(2)—C(1)	1·384(6)	C(1)—C(2)—C(3)	118·8(4)
C(6)—C(1)	1·384(6)	C(2)—C(1)—C(6)	121·2(3)
C(3)—C(2)	1·385(6)	C(1)—C(6)—C(5)	118·9(4)
C(4)—C(3)	1·370(6)	C(2)—C(3)—C(4)	120·3(4)
C(5)—C(4)	1·374(7)	C(3)—C(4)—C(5)	120·6(4)
C(6)—C(5)	1·382(6)	C(4)—C(5)—C(6)	120·2(4)
N(1)—C(7)	1·307(5)	C(2)—C(1)—S	119·6(3)
N(2)—C(7)	1·315(4)	C(6)—C(1)—S	119·2(3)
N(2)—C(8)	1·466(6)	C(7)—N(1)—S	117·9(3)
N(2)—C(9)	1·466(5)	N(1)—C(7)—N(2)	122·7(3)
S—C(1)	1·772(3)	C(7)—N(2)—C(8)	121·5(3)
S—N(1)	1·612(3)	C(7)—N(2)—C(9)	121·2(3)
S—O(1)	1·437(3)	C(8)—N(2)—C(9)	117·3(3)
S—O62)	1·449(3)	C(1)—S—N(1)	104·1(2)
		C(1)—S—O(1)	107·1(2)
		C(1)—S—O(2)	107·3(2)
		N(1)—S—O(1)	112·9(2)
		N(1)—S—O(2)	106·8(2)
		O(1)—S—O(2)	117·6(2)

An amidine skeleton is substituted at N(2) by two methyl groups, which increase the electron-donating property of the N(2) atom, whereas at N(1) the sulphone group SO_2Ph is substituted. This group is strongly electron accepting and hence the push–pull system is formed with NMe_2 as the donating group. As a result, one observes equalization of the CN bond length, which may be rationalized by two effects: (i)

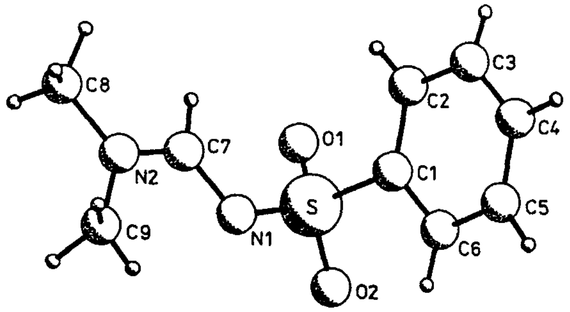
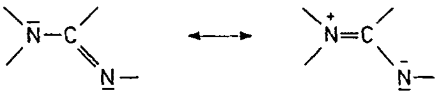
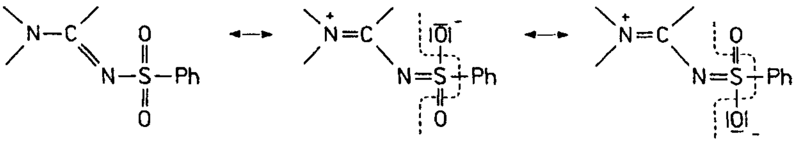


Figure 1. Structure of the molecule with the numbering of the atoms

n–π conjugation, described by canonical structures I and II, and (ii) through-conjugation effect (structures III–V).



I II



III IV V

Application of the HOSE model[5] to the amidine skeleton allows us to estimate the weights of two canonical structures, yielding in I = 53·0% and II = 47·0%. If the conjugation scheme is extended to include sulphur on the right of the scheme indicated by dotted line, these weights are III = 56·1% and IV + V = 43·9%. In this way shortening of the N=C bond is taken into account but not effects on the two SO bonds. However, in this way in both schemes there are equal numbers of canonical structures, since IV and V are taken together. Hence comparison of these two pictures is permitted. Both of these pictures are qualitatively very close to each other. A decrease of %(IV + V) in comparison with %(II) is associated with the nature of the C—S bond, which is much longer than for atoms in the second group of the Periodic Table, resulting in a weaker inclination for π-electron delocalization. To apply the HOSE model for a system with an NS bond, the model had to be extended by including parameters for NS bonds, which are collected in Table 4. The parameters adopted here for the force constants for NS bonds are very approximate, since the values from CS bonds[17] were taken for further calculation. In spite of this, the general picture is reasonably acceptable. The conclusion that may be drawn is that the through-resonance effect does not seem to be important in the case under study. This is in line with previous findings[18–20] that in most cases either this effect is really weak or, if it is not weak, the pulling and pushing groups have to be extremely strong (e.g. as in *p*-nitrosophenolate anion).[21]

Table 4. Hose parameters for NS bond

Bond	Bond length (Å)	Force constant
NS single[a]	1·651(3)	5·16
NS double[b]	1·521(3)	8·87

[a] Taken from electron diffraction (ED) geometry of *N,N,N′,N′*-tetramethylsulphonyldiamide.[15]

[b] taken from ED geometry of *S,S*-dimethylsulphoximide.[16]

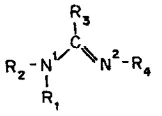
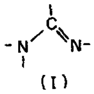
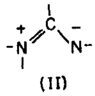
In order to illustrate the problem of substituent effects on the π-electron structure in the amidine skeleton, Table 5 gives the weights of canonical structures I and II for amidine derivatives for which a direct comparison can be made. Two derivatives of formamidine, i.e. our structure (**1**) and *p*-nitrophenyl-N^1-formamidine, are compared. The much stronger electron-attracting power of SO_2Ph compared with $PhNO_2$ results in a greater delocalization of π-electrons in the first case, and %(I) and %(II) are much closer to 50% in this case.

Now one can analyse the effect of substitution at a functional carbon. In the series of three compounds (Table 5) N^1, N^1-dimethyl-N^2-*p*-nitrophenylformamidine (**2**), N^1, N^1-dimethyl-N^2-*p*-nitrophenylacetamidine (**3**) and N^1, N^1-dimethyl-N^2-*p*-nitrophenyl-2,2-dimethylpropanamidine (**6**), with an increase in the size of the substituent at the functional carbon we observe an increase in π-electron localization. This may be directly described by the difference

$$\Delta = \%(\mathrm{I}) - \%(\mathrm{II})$$

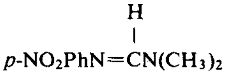
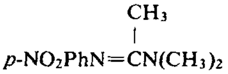
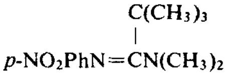
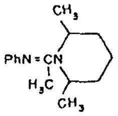
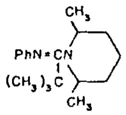
For the sequence mentioned above we find that Δ increases from 33·6 and 34·4 for **2**, to 43·4 and 62·0 for **3** and 70·4 for **6**. An interesting comment on this

Table 5. Weights of canonical structures I and II for a series of amidine derivatives

							Δ^a	Ref.
No.	R_2	R_2	R_3	(R_4	(%)	(%)		
1	Me	Me	H	SO_2Ph	53·0	47·0	6·0	This work
2	Me	Me	H	p-NO_2Ph	67·2 66·8	32·8 33·2	34·4 33·6	9
3	Me	Me	Me	p-NO_2Ph	71·7 81·0	28·3 19·0	43·4 62·0	9
4	H	p-MePh	Me	p-MePh	83·0	17·0	86·0	22
5	Me	Ph	Me	p-NO_2Ph	84·0	16·0	88·0	23
6	Me	Me	C(Me)$_3$	p-NO_2Ph	85·2	14·8	70·4	9
7	2,6-*cis*-Dimethylpyridyl		Me	Ph	85·8	14·2	71·6	24
8	2,6-*cis*-Dimethylpyridyl		C(Me)$_3$	Ph	96·8 98·6	3·2 1·4	93·4 97·2	24

[a] Δ is a numerical measure of π-electron localization; Δ = 100 represents a fully localized π-electron system.

Table 6. Comparison of bond lengths in substitution at the functional carbon by various substituents, with increasing bulkiness

No.	Substituent	C=N (Å)	C—N (Å)	Ref.
1	 $p\text{-}NO_2PhN{=}\overset{H}{C}N(CH_3)_2$	1·289(4) 1·289(4) Mean: 1·289	1·332(4) 1·331(4) 1·3315	9
2	 $p\text{-}NO_2PhN{=}\overset{CH_3}{C}N(CH_3)_2$	1·281(5) 1·294(5) Mean: 1·2875	1·354(6) 1·346(5) 1·350	9
3	 $p\text{-}NO_2PhN{=}\overset{C(CH_3)_3}{C}N(CH_3)_2$	1·293(3)	1·380(3)	9
4	 (MA)	1·278(3)	1·374(3)	24
5	 (TBA)	1·263(5) 1·262(5)	1·441(5) 1·424(5)	24

finding comes from analysis of the CN bond lengths in these three systems. The relevant data are given in Table 6. It can be seen that the shorter CN bond, say the double bond, is hardly affected by substitution at the functional carbon. Its bond lengths vary between 1·2875 Å (mean value for **3**) and 1·293(3) Å for **6**. The differences are insignificant (less than 3α). However, the situation for the longer CN bond, say the single bond is different: it varies from 1·3315 Å (mean value for **2**), through 1·350 Å for **3** to 1·380(3) Å for **6**. Evidently replacing H by CH_3 and finally by *tert*-butyl groups changes the single CN bond lengths substantiality. This finding is in line with earlier observations,[9,24] where decoupling of the amidine π-system and the 2p orbital of the imine N atom due to steric hindrance of the bulky substituent at the functional carbon was postulated. When an electron-accepting substituent, *p*-NO_2Ph in cases **2**, **3** and **6**, is replaced with phenyl,[24] the localization effect is still greater and the Δ value increases to 1·6 for MA (2,6-*cis*-dimethylpiperidyl- *N*-phently-acetamidine) and 93·4 and 97·2 for two independent molecules of TBA (2,6-*cis* -dimethylpiperidyl-*N*-phenyl-2,2-dimethylpropionamide).

Our results are in full agreement with those of Gilli and Bertolasi,[24] but the main advantage of our work is that by using the HOSE model and the Δ value the conclusions about π-electron localization may be expressed in a more quantitative manner.

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