INVERSION OF CONFIGURATION IN THE AMINOLYSIS OF N-BENZENESULFONYLBENZIMIDOYL CHLORIDE. CRYSTAL AND MOLECULAR STRUCTURE OF N^2-BENZENESULFONYL-N^1-(3-NITROPHENYL)BENZAMIDE

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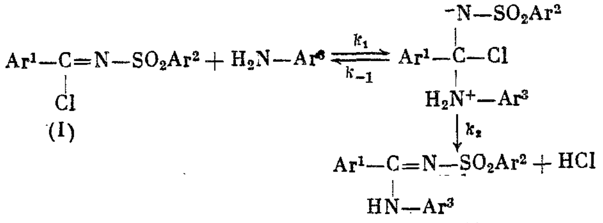
We have previously reported kinetic evidence [1] in favor of a mechanism involving addition—elimination with dissociation of a tetrahedral intermediate product (TIP) as the slow step in the reactions of N-arylsulfonylbenzimidoyl chlorides with aromatic amines in aprotic reaction media:



$Ar^1 = Ar^2 = C_6H_5$(I), $Ar^1 = Ar^2 = C_6H_5$(II), $Ar^3 = 3\text{-}NO_2—C_6H_4$.

In order to investigate the stereochemistry of this reaction, we have carried out an x-ray structural analysis of the final product (II).

EXPERIMENTAL

N^2-Benzenesulfonyl-N^1-(3-nitrophenyl)benzamidine (II) was formed in quantitative yield by the reaction of 3-nitroaniline with N-benzenesulfonylbenzimidoyl chloride (I) in acetonitrile. Based on TLC analysis (Silufol UV-254, $CHCl_3$ eluent, R_f 0.2) the reaction product is not changed during the isolation and purification processes. Pale yellow crystals, mp 184-185.5°C. PMR spectrum (dimethylacetamide, TMS standard, δ, ppm): 11.05 s (N—H), 8.98 t (proton in the 2-position of the 3-nitrophenyl group), 8.37-7.43 (C_6H_5), intensity ratio 1:1:13. IR spectrum (KBr pellet, ν, cm^{-1}): 545, 575, 690, 740, 940, 1095, 1155, 1290, 1330, 1430, 1545, 3400. Found: C 59.81; H 4.05; N 11.15; S 8.26%. $C_{16}H_{15}N_3O_4S$. Calculated: C 59.83; H 3.96; N 11.02, S 8.41%.

Crystals of (II) in the form of transparent prisms were monoclinic at 20°C, with a = 7.500(1), b = 20.377(2), c = 12.305(2) Å, β = 108.019(9)°, Z = 4, d_{calc} = 1.42 g/cm^3, $P2_1/c$ space group. The unit cell parameters and intensities of 1753 reflections with $I \geq 2\sigma$ were measured on a Hilger—Watts automated four-circle diffractometer (λMoK_α, graphite monochromator, $\theta/2\theta$ scanning, $\theta \leq 30°$). The structure was solved using direct methods and refined by full matrix least squares with anisotropic (thermal) approximations for all nonhydrogen atoms. All of the H atoms were visualized in a difference Fourier series and refined with fixed B_{iso} values equal to 4 Å^2. The final R values were R = 0.042, R_w = 0.040. All calculations were performed on an Eclipse S/200 computer using the INEXTL system of programs [2]. The nonhydrogen atom coordinates are summarized in Table 1; the hydrogen atom coordinates can be obtained from the authors.

A solution of 0.1060 g (II) in 10 ml purified chlorobenzene was heated at reflux for 5 h while irradiating it with an OKN-11 lamp. The light yellow solution turned red. According to TLC analysis (Silufol UV-254, $CHCl_3$ eluent), the mixture contains the starting amine (R_f 0.2) and a very small amount of a highly colored substance, which migrates with the solvent front. The reaction mixture was passed through a column with aluminum oxide (with dioxane as eluent). The solvent was evaporated from the colored fraction to give 0.0911 g (86% of the charged amount) of reddish crystals. Recrystallization from alcohol gave 0.0816

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TABLE 1. Nonhydrogen Atom Coordinates (× 10^4, × 10^5 for S)*

Atom	x	y	z	Atom	x	y	z
S^1	78117(11)	71739(4)	5715(8)	C^7	11849(4)	8083(2)	−346(3)
O^1	5988(3)	6887(1)	58(2)	C^8	7692(4)	8002(1)	152(3)
O^2	8580(3)	7136(1)	1785(2)	C^9	8408(5)	8487(2)	952(3)
O^3	6332(3)	5055(1)	−2055(3)	C^{10}	8332(6)	9132(2)	578(4)
O^4	7544(4)	4109(1)	−2089(3)	C^{11}	7555(6)	9277(2)	−552(4)
N^1	9140(3)	6777(1)	−35(2)	C^{12}	6839(5)	8792(2)	−1339(3)
N^2	11850(3)	6561(1)	−447(2)	C^{13}	6914(4)	8153(2)	−993(3)
N^3	7680(4)	4697(1)	−1933(3)	C^{14}	11481(4)	5918(1)	−862(3)
C^1	10818(4)	6966(1)	−10(3)	C^{15}	9712(4)	5632(1)	−1208(3)
C^2	11790(4)	7596(1)	423(3)	C^{16}	9552(4)	4998(1)	−1581(3)
C^3	12716(5)	7669(2)	1569(3)	C^{17}	11034(5)	4617(2)	−1637(3)
C^4	13709(5)	8243(2)	1957(3)	C^{18}	12769(4)	4911(2)	−1308(4)
C^5	13745(5)	8724(2)	1203(4)	C^{19}	13011(4)	5549(2)	−936(3)
C^6	12836(5)	8653(2)	58(4)				

*Temperature factor and bond length values, as well as bond angles, can be obtained from the authors.

g (77% of charge) of light yellow crystals, mp 182-184°C. Repeat crystallization of 0.0653 g gave 0.0449 g of product, mp 184-185.5°C. Its IR spectrum was identical to that of an authentic sample.

RESULTS AND DISCUSSION

The starting material (I) is known only in the Z-configuration [3]. Upon treatment of (I) with excess 3-nitroaniline in acetonitrile a single reaction product (II) is obtained, having the E-configuration. Attempts to prepare the Z-isomer of (II) by heating and UV irradiation failed (under conditions in which imidates are readily isomerized [4]). Apparently the E-isomer which is obtained via this reaction is more thermodynamically stable than the Z-isomer. There have been reports in the literature concerning the predominant E-configuration of amidines [5], although the structural assignments were made using qualitative methods.

Two examples are known [4, 6] of nucleophilic substitution reactions in the series of imidoyl halides involving O-nucleophiles; an addition–elimination mechanism has been proposed for these reactions. It is assumed that the slow step in these reactions involves attack of the nucleophile ($k_{-1} < k_2$), and in both examples retention of configuration throughout the substitution process has been confirmed. The authors [4, 6] have explained these results within the concept of "stereoelectronic control" [7], which for the indicated systems means kinetic control: Z-imidates are formed rapidly, even though E-isomers of imido esters are thermodynamically more stable. In our case the situation is different: the TIP which is formed undergoes elimination to give the starting materials more rapidly than elimination to products ($k_{-1} > k_2$, [1]). As might be expected, therefore, in this type of case internal rotation (transmutation) occurs faster than elimination ($k_{rot} > k_{-1} > k_2$ [8]), so there are no impediments to achieving thermodynamic reaction control. The mechanism outlined above is therefore capable of explaining completely the stereochemical results. The alternative mechanism which is frequently considered for this type of reaction involves simultaneous or synchronous substitution at the sp^2-hybridized carbon atom and would be accompanied by retention of configuration [8]; it is therefore less reasonable in this case.

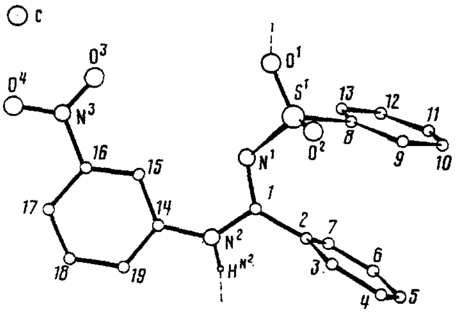

Fig. 1. General view of a molecule of (II).

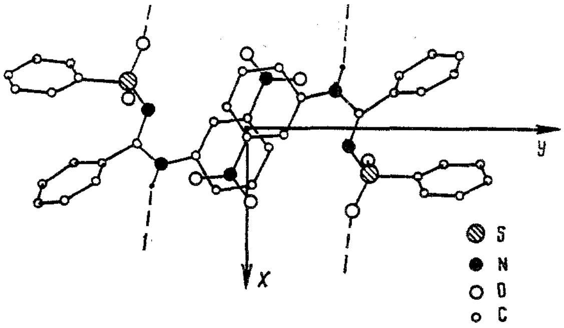

Fig. 2. Projection fragment structure of (II) in the XOY plane.

The formation of the E isomer in this reaction was demonstrated unequivocally by x-ray structural analysis of the reaction product (II). A general view of a molecule of (II) is shown in Fig. 1.

The S atom in (II) exists in a conventional, nearly tetrahedral bond configuration. The difference in the S^1-O^1 (1.441(3)) and S^1-O^2 bond lengths (1.427(2) Å) can be attributed to participation of the O^1 atom in intermolecular hydrogen bond formation. The S^1-C^8 bond distance of 1.758(3) Å agrees very well with that observed earlier by us for compound (I) (1.758Å) and also with the calculated average of 1.756 Å presented in [9] for S(VI)—Ph bonds. The orientation of the benzene ring at C^8-C^{13} is such that the O^2 atom is located in the same plane with it: the $O^2S^1C^8C^9$ torsional angle is equal to 4.3(3)°. The values of the $C^1N^1S^1C^8$ (50.6(3)°) and $C^{13}C^8S^1N^1$ (62.2(3)°) torsional angles cannot be interpreted in such a way that the sulfonyl group geometry can be assigned to either of the ideal types of sulfone conjugation schemes described in [10]; the same was true of (I).

We had previously postulated [1] that the effect of the electronic nature of the substituent attached to C^1 on the $C^1{=}N^1$ and N^1-S^1 bond length values was similar to the effect predicted for sulfeneketimine molecules on the basis of quantum mechanical calculations [11]. In comparison with molecules of (I), in (II) the electron withdrawing halogen substituent has been replaced by an amino group, which is electron donating in character. The changes observed in the geometry of (II) which are associated with this substitution change are consistent with those anticipated in analogy with the sulfeneketimine model: the $C^1{=}N^1$ bond length is increased to 1.307(4) (vs. 1.281 Å in (I)), while the S^1-N^1 distance is decreased to 1.633(3) (vs. 1.660 Å in (I)).

The E configuration relative to the $C^1{=}N^1$ bond in (II) leads to the appearance of several short intramolecular contact distances, $C^2 \ldots S^1$ 3.164(3), and $C^2 \ldots C^8$ 3.100(5) Å, which in turn lead to an increase in the $N^1C^1C^2$ bond angle to 128.5(3)°. We should note, however, that the angle around the N^1 atom is somewhat contracted relative to that observed in (I) (124.2(2) vs 126.0°, respectively), whereas the deviation of the S atom from the plane of the $C^1{=}N^1$ double bond, i.e., the $N^1N^2C^1C^2$ plane, which is fulfilled in (II) to an accuracy of 0.008(3) Å, is approximately the same in the two cases, −0.160(1) in (II) and 0.128 Å in (I). In contrast to the molecular structure of (I), in which the Ph substituent attached to C^1 lies within the plane of the double bond and is therefore involved in conjugation with it, in (II) the plane of the benzene ring at C^2-C^7 forms a dihedral angle of 99.4° with the plane of the $C^1{=}N^1$ double bond, and so the C^1-C^2 bond length of 1.492(4) Å is longer than that observed in (I) (1.465 Å). In the molecular structure of (II) it is the unshared electron pair attached to the N^2 atom which lies in the plane of the $C^1{=}N^1$ double bond and which is thus involved in conjugation with its π-system. This is confirmed by the difference in the N^2-C^1 (1.350(4) Å) and N^2-C^{14} (1.402(4) Å) bond lengths with the sp^2-hybridized carbon atoms. The plane of the benzene ring at $C^{14}-C^{19}$ forms a dihedral angle of 17.5° with the plane of the $N^1{=}C^1$ double bond. This type of conformation is apparently stabilized by electrostatic interaction of the H^{15} hydrogen atom with the unshared electron pair on N^1: the $N^1 \ldots H^{15}$ distance is 2.25(3) Å, $N^1 \ldots C^{15}$ 2.844(4) Å, and the $C^{15}-H^{15} \ldots N^1$ angle equal to 122(1)°. The plane of the nitro group forms a dihedral angle of 11.7° with the plane of the benzene ring. Using the benzene ring at $C^{14}-C^{19}$ as an example, the effect of the electronic nature of the substituent on its geometry is very clear: the endocyclic angle at the C^{14} atom containing the electron donating amino substituent is decreased to 118.6(3)°, while that around C^{16} with the electron withdrawing nitro group substituent is increased to 124.3(3)°.

Molecules of (II) are associated with one another in the crystal structure via weak $N^2-H^{N2}...O^1$ (1 + x, y, z) hydrogen bonds ($N^2...O^1$ 3.044(3) Å, $H^{N2}...O^1$ 2.19(3) Å, $N^2-H^{N2}...O^1$ angle 169(1)°) along the x axis. It is clear from Fig. 2 that adjacent chains are also associated pairwise with one another by means of so-called "stacking" interactions (nonbonding dispersion interactions between aromatic systems oriented parallel to one another) between the nitrophenyl rings at $C^{14}-C^{19}$ of neighboring molecules, via a center of symmetry of the type 0.1/2.0. The distance between the planes of the nitro groups and the centers of the benzene rings located on top of them is 3.67 Å, while the shortest distance $C^{15}...C^{16}$ between atoms of benzene rings which are superimposed on one another with strong shifts is 3.544(4) Å.

CONCLUSIONS

The E-molecular configuration of N^2-benzenesulfonyl-N^1-(3-nitrophenyl)benzamidine has been verified by x-ray structural investigation, which also made it possible to confirm the addition—elimination mechanism which had been proposed earlier for the reactions of N-arylsulfonylbenzimidoyl chlorides with aromatic amines in aprotic reaction media. Molecules of (II) are associated with one another in the crystal structure via H-bonds in a chain, while neighboring chains are associated with one another by means of the so-called "stacking" interactions.

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