Heteroatom Chemistry
Volume 15, Number 3, 2004

The First General Synthesis of 3-Iodo-4-*R*-furazans

Aleksei B. Sheremetev,[1] Julia L. Shamshina,[1] Dmitry E. Dmitriev,[1] Denis V. Lyubetskii,[2] and Mikhail Yu. Antipin[2]

[1]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47, Leninsky Prosp., Moscow 119991, Russia*
[2]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov Street B-334, Moscow 119991, Russia*

Received 19 December 2003; accepted 8 January 2004

ABSTRACT: *The first general synthetic route has been developed for the convenient preparation of iodofurazans. The approach was accomplished by one-pot diazotization-iodation reaction of appropriate aminofurazans. A combination of sodium nitrite and iodine in organic solvent under anhydrous conditions as the reaction conditions allowed to solve problem in iodofurazans preparation. The investigation of the substituent's influence on NMR data of the iodofurazans has been carried out. The X-ray crystal structure of the 3-amino-4-iodofurazan* **1d** *is reported.* © 2004 Wiley Periodicals, Inc. Heteroatom Chem 15:199–207, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20007

INTRODUCTION

Iodo heterocycles are building blocks in organic chemistry due to the reactivity of the iodine substituent toward different reagents. Among various methods for the preparation of iodo heterocycles, diazotization reaction of corresponding amino derivatives is the most widely used. The amino group can be replaced by iodine and by many other groups found in aqueous diazonium ion reactions.

Despite a relatively large number of known furazan derivatives, there are only two with iodine at the ring [1]. Thus, the first report of an iodofurazan was the synthesis of the parent 3-iodofurazan by reduction of 3,4-diiodofuroxan with SO_2 in ethanol described by Birckenbach and Sennewald in 1931 [2] As late as 1993, second and final compound, 3-iodo-4-methylfurazan **1a**, was prepared by diazotization of 3-amino-4-methylfurazan **2a** with $NaNO_2/H_2SO_4$ followed by treatment with aqueous solution of NaI; no iodo product could be obtained when other aminofurazans were exposed to the same reaction conditions [3]. A ring-cleavage reaction and triazene formation usually occurred when aminofurazans were diazotized under ordinary conditions [1,4]. Until now, no general methods for the direct transformation of the NH_2-group at furazan ring to a halogen have been reported.

Iodofurazans are potential precursors to new derivatives through the use, for example, of palladium-catalyzed coupling reaction or halogen-metal exchange reactions, oxidation, and other transformations. In the context of developing a synthetic methodology for halofurazans [5], we focused on iodofurazans **1**. Clearly attractive precursors for the synthesis are available aminofurazans [1]. However, aminofurazans are weak bases [6]. It is known that diazotization reactions of weak based aryl and hetaryl amines are problematic [7].

Correspondence to: Aleksei B. Sheremetev; e-mail: sab@ioc.ac.ru.
Contract grant sponsor: Russian Foundation for Basic Research.
Contract grant number: N° 1-03-32944.

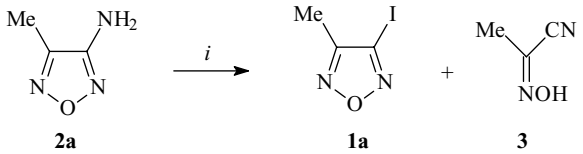
Because aqueous diazotization reaction of aminofurazans usually gave no desired products, an alternate route was required. From our viewpoint the most attractive procedure involves the unaqueous diazotization reaction. Relatively little works have been reported on such processes. Thus, heating (80–110°C) of a variety of amines (anilines [8], aminopyrimidines [9], aminoimidazoles [10]) with alkyl nitrite in diiodomethane was reported to give the respective iodo derivatives in moderate yields. In this process, a free radical is apparently generated by the homolysis of initially formed diazonium compound, followed by conversion to (het)aryliodide by iodine abstraction from the solvent. Herein we report a general synthetic partway to iodofurazans resulting from utilization of an optimized unaqueous diazotization reaction for aminofurazans.

RESULTS AND DISCUSSION

Synthesis

In our case, however, similar diazotization-iodation procedure with 3-amino-4-methylfurazan **2a** afforded only little iodo product **1a** (GLPC yield was 18%). The major product was α-hydroxymino acetonitrile **3** (65%) (Scheme 1). Moreover, properties of iodofurazan **1a** and CH_2I_2 are resembling each other and isolation of the product **1a** proved to be difficult.

It has been reported in the literature that iodobenzene can be prepared by reaction of aniline with amyl nitrite and iodine at refluxing in benzene or CCl_4 [11]. Encouraged by this report, we chose to examine a synthesis of iodofurazan **1a** by diazotization-iodation of amine **2a** with iodine using a variety of different alkyl nitrites and solvents. Upon reaction of **2a** with iodine (1 equiv) at room temperature using *i*-Amyl-ONO (1.5 equiv) in MeCN, a 62% GLPC yield of **1a** was obtained. However, separated yield of **1a** was only 22%. Use of *i*-Pr-ONO provided **1a** in 65% GLPC yield and only 26% separated yield. Changing of the solvent to glyme, with *i*-Pr-ONO as diazotization agent, reduced the separated yield to 15%. When *i*-Pr-ONO in ethyl acetate was employed, attempts to separate **1a** were unsuccessful. All reactions were diluted with CH_2Cl_2, washed with H_2O, dried and evaporated. Product **1a** was isolated by chromatographic purification. There are difficulties associated with high volatility of the product. Thus, in special experiment, a solution of **1a** (1 g) in 30 ml CH_2Cl_2 was evaporated at room temperature at reduced pressure. The only 0.6 g (60%) of starting compound remained in the flask! Additives (ca. 5%) of alkyl nitrites and alcohols in CH_2Cl_2 increased the disappearance of **1a** up to 50–80%. When $CHCl_3$ was employed as a solvent, only 22% of **1a** was store. Additionally, an attempt to improve the separation, using a high-boiling solvent, such as nitrobenzene, and evaporation of volatile product (GLPC yield was 47%) failed to yield the expected iodo derivative **1a** since the compound decomposed at heating.



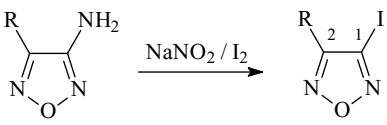
SCHEME 1 *Reagents and conditions*: *i*, i-Amil-ONO/CH_2I_2, 80°C, 1 h.

Because the increased volatility had been observed for iodo derivative **1a** especially in the presence of alkyl nitrites and corresponding alcohols, attention was turned toward the diazotization by a reagent free of an organic fragment.

We found that amine **2a** underwent smooth diazotization-iodation reaction with a mixture of iodine and $NaNO_2$ in acetonitrile to give iodofurazan **1a** (Scheme 2). The reaction was initially performed by addition of solid **2a** and $NaNO_2$ to the I_2 solution in MeCN at ca. 5°C; however for ease of the reaction, addition of the solid $NaNO_2$ to a slurry of **2a** and I_2 in MeCN/CH_2Cl_2 mixture at room temperature was preferred. The product was isolated by chromatographic purification.

This methodology has been successfully applied for the synthesis of a number of iodofurazans **1b–g** (Scheme 2). The reaction of aminofurazans **2b–g** with iodine and $NaNO_2$ in MeCN/CH_2Cl_2 mixture occurred readily at room temperature over a period of 2–3 h. The products yields are shown in table.

The transformation is successful in the presence of a variety of functional groups. It is interesting

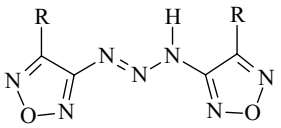


Product	**R**	*GLPC Yield (%)*	*Separated Yield (%)*
1a	Me	56	35
1b	Et	52	38
1c	OMe	64	29
1d	NH_2	27	21
1e	Br	51	28
1f	I	55	37
1g	Ph	48	35

SCHEME 2

to note that the only an amino group of 3,4-diaminofurazan **2d** was transformed to iodine group to give 3-amino-4-iodofurazan **1d**. However, pure 3-amino-4-iodofurazan **1d** subjected to the reaction was readily converted to 3,4-diiodofurazan **1f**. This suggests that some species formed in the diazotization-iodation of diamine **2d** inhibited reaction of compound **1d**. However, attempted diazotization-iodation of aminofurazans bearing strong electron-withdrawing substituents (3-amino-4-nitrofurazan, 3-amino-4-cyanofurazan, 4,4′-diaminoazo-, and azoxyfurazans) under these conditions failed to give the corresponding iodofurazans. This clearly illustrated the importance of the electronic properties of the substituent at furazan ring in the diazotization process.

A byproduct, corresponding 1,3-*bis*(3-*R*-furazan-4-yl) triazene **4**, was observed at preparation of the iodofurazans bearing electron donating substituents; triazenes formation is a well documented side-reaction for aminofurazans diazotization [1]. The solubility of these triazenes in nonpolar solvent is quite limited; simple filtration of a solution of the reaction products through a short SiO_2 pad is effective to separate the byproduct.



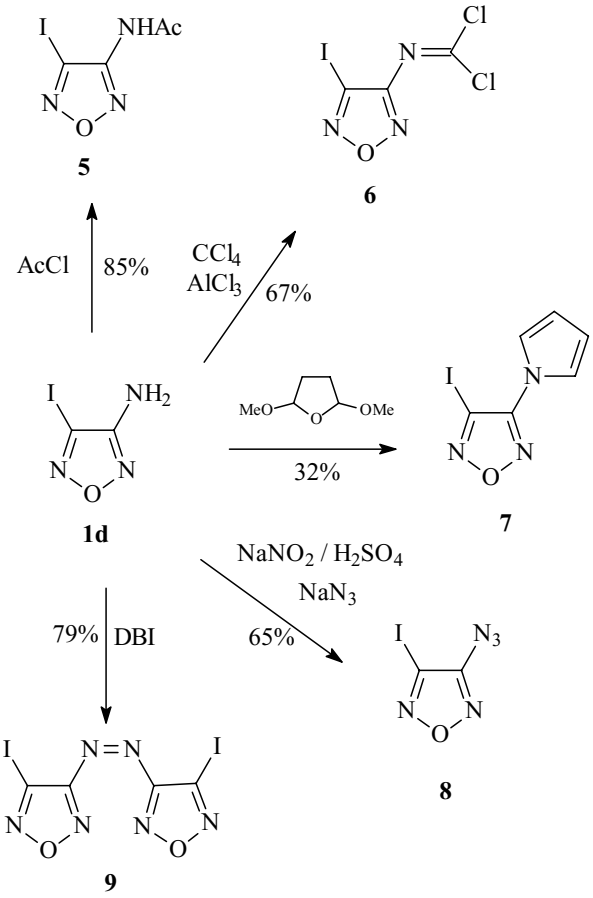
4

This diazotization-iodation procedure does not require harsh reaction conditions or difficult to handle reagents and can be easily scaled up to the preparation of gram quantities of the iodofurazans.

Compounds **1a–f** are usually solids at room temperature or slight cooling, but they are volatile liquids after melting point. The purification can be achieved by sublimation. The iodofurazans are light-sensitive; at light they decompose with the release of I_2. The iodofurazans are soluble in common organic solvents and they are stable to solvolysis by MeOD in DMSO-d_6 at room temperature over a period of 3 days.

Scheme 3 demonstrates some of the synthetic potential of amine **1d** for preparation of various iodofurazans. It reacted smoothly with acetyl chloride at room temperature to give the amide **5**, with carbon tetrachloride under $AlCl_3$ promotion to give dichloroimine **6** [12]. The synthesis of pyrrole **7** was achieved by Clauson-Kaas reaction [13].

Diazotization of amine **1d** could easily be accomplished by nitrosylsulfuric acid followed by treatment with an aqueous solution of sodium azide to



SCHEME 3

give compound **8** [3]. No characterizable product could be obtained when the amine **1d** was exposed to oxidation with $KMnO_4$ under acidic reaction conditions [1]. In sharp contrast to this result, the amine **1d** reacted with the dibromoisocyanurate (DBI) [14] in an organic solvent to give the desired azofurazan **9** (Scheme 3).

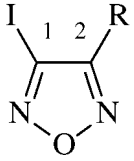
MS Data

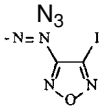
The electron impact mass spectra showed, for all iodofurazans, molecular ion peak (rel intens 20–35%), diagnostic fragment corresponding to the loss of iodine, giving rise to signals with *m/z* values for (M-127) (65–75%) and a strong iodine ion peak at *m/z* 127 (100%). In the case of the compounds **1a–d**, the spectra also revealed others diagnostic peaks corresponding to the loss of NO [15], affording signals with *m/z* value for (M-30) and (M-127-30).

NMR Investigation

The structure of the iodofurazans was confirmed on the basis of a detailed NMR analysis. Assignments

TABLE 1 Chemical Shifts δ NMR ^{13}C and SCS Values for Iodofurazans in $CDCl_3$



		C(2)		C(1)		
Compound	*R*	*δ (ppm)*	*SCS$_i^a$*	*δ (ppm)*	*SCS$_o^a$*	*R [δ (ppm)]*
1a	Me	155.3	9.2	105.5	0.7	9.4
1b	Et	159.4	15.6	104.5	−0.5	11.7 (Me), 18.1 (CH_2)
1c	OMe	167.1	31.4	95.7	−14.4	59.6
1d[b]	NH_2	159.8	18.2	102.1	−13.4	–
1e	Br	141.0	−6.8	108.4	3.2	–
1f	I	114.3	−34.1	114.3	8.9	–
1g	Ph	156.8	13.1	102.5	−1.1	124.7 (*i*), 128.7, 129.0 (*o*, *m*-), 131.1 (*p*-)
5[b]	NHAc	155.1	9.5	106.7	−8.1	22.9 (Me), 169.0 (C=O)
6	N=CCl_2	158.4	15.7[c]	100.3	–	140.9 (CCl_2)
7		154.4	11.9	95.6	−8.3	112.5 (b), 120.3 (a)
8	N_3	158.0	12.0	97.2	−9.1	–
9		162.8	21.0[c]	99.0	–	99.0, 162.8
10 [16]	NO_2	162.3	19.5	95.1	−4.9	–

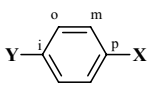
[a]The values of the substituent constants are from Ewing review [17].
[b]In DMSO-d_6.
[c]SCS_i values are calculated by [Eq. (2)].

of ^1H signals were made using considerations of splitting patterns and additivity of chemical shifts. The ^{13}C NMR spectra were assigned by intensity, peak multiplicity under off-resonance decoupling, and substituent chemical shifts (SCS) considerations (Table 1). The ^1H and ^{13}C chemical shifts of the compounds are considered to be accurate to 0.02 and 0.05 ppm, respectively.

Correlation of ^{13}C chemical shifts of carbon atoms of the furazan ring in iodofurazans with the SCS values of corresponding monosubstituted benzenes (Fig. 1) were performed using Lynch [18] equation [Eq. (1)]

$$\text{Shift}_x(\text{Y}) = a + b \times \text{SCS}_x(\text{H}) \qquad (1)$$

The correlation of ^{13}C chemical shifts in 1,4-disubstituted benzenes [Shift_x(Y)] with the SCS values of monosubstituted benzenes [SCS_x(H)] showed that the fixed substituent (Y in **11**) has an effect on its carbon of attachment [17]. This is measured by the slope b of the Lynch equation [Eq. (1)]



11

Recently, we reported [13,19,20] the range of successful correlations established on this basis for ^{13}C chemical shifts in the furazan series. The Lynch correlation of ^{13}C chemical shifts for carbon atom of the furazan ring bearing variable substituent R in iodofurazans **1** has a slope b of 0.84, indicating that the substituent effect significantly diminished in iodofurazans compared to monosubstituted benzenes.

$$\delta(\text{C}_2)(\text{R}) = a + b \times \text{SCS}(\text{R}) \qquad (2)$$
$$a = 145.2 \pm 0.8$$
$$b = 0.84 \pm 0.04$$
$$(r = 0.990,\ n = 10)$$

The above result agrees well with our previous correlations that showed the absence of significant polarization of the furazan ring under substituent influence. Analysis of ^{13}C chemical shifts for carbon of the furazan ring bearing iodo group (C1) do not afford good Lynch correlation.

It should be noted that the iodofurazans **1a–f** show the diagnostic chemical shift for quaternary carbon of the furazan ring bearing iodo group in δ 95–114 ppm region.

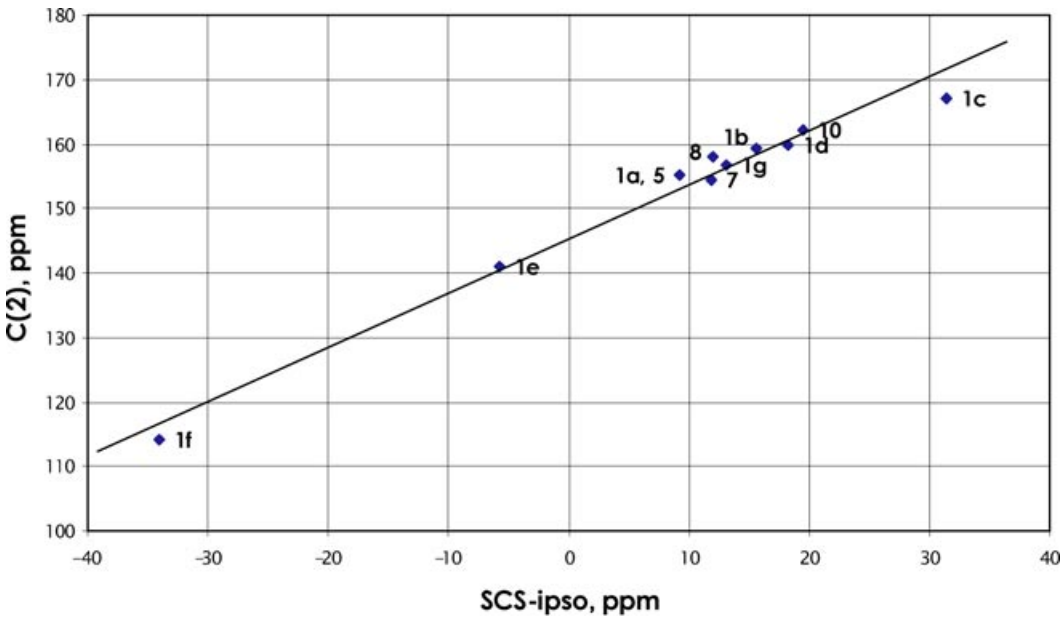


FIGURE 1 Plot of chemical shifts (δ) of carbon 2 in iodofurazans vs SCS_i values for monosubstituted benzenes.

X-ray Crystallography

Single crystals of 3-amino-4-iodofurazan **1d** (Fig. 2) were grown by slow evaporation of $CHCl_3$ solution. Bond angles and bond lengths are given in Table 2. Molecular geometry for both independent molecules is as expected, but some features may be noted. Thus double bond C(1)—N(1) at iodine group is slightly shorter than C(2)—N(2) at the amino group, while the C—C single bond is slightly elongated. This may be attributed to the donor-acceptor nature of the substituents as well as steric repulsion between the NH_2 group and the iodine atom. In agreement with earlier reports the length of the N(1)—O(1) bond, proximate to electron-withdrawing substituent, is equal to 1.399 Å, while the length of the N—O bonds closest to amino group (an electron donor) is shortened to 1.389 Å.

Analysis of the crystal packing has revealed that molecules in crystal are assembled in layers due to H-bonding and secondary interactions of the iodine with nitrogen atoms of the furazan rings (Fig. 3). The H-bonding system is different for two independent molecules. For the first molecule, both hydrogen atoms of the amino group are strongly bounded with nitrogen atoms of surrounding furazans (H...N 2.27 and 2.28 Å, N...N 3.11 and 3.23 Å, N—H...N

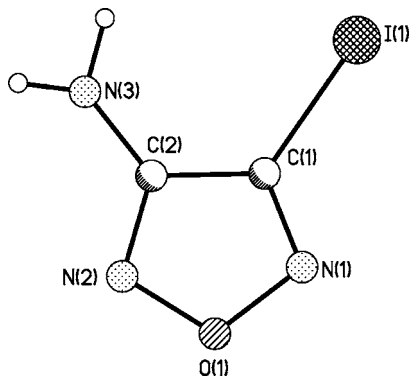


FIGURE 2 The general view of **1d.**

TABLE 2 Bond Lengths (Å) and Angles (°) for **1d**

Bond	*Å*	*Angle*	°
I(1)–C(1)	2.068(6)	N(2)–C(2)–N(3)	125.4(6)
C(2)–N(2)	1.334(8)	N(2)–C(2)–C(1)	107.3(6)
C(2)–N(3)	1.367(9)	N(3)–C(2)–C(1)	127.3(6)
C(2)–C(1)	1.445(8)	C(1)–N(1)–O(1)	105.5(6)
N(1)–C(1)	1.284(9)	N(1)–C(1)–C(2)	110.7(6)
N(1)–O(1)	1.399(7)	N(1)–C(1)–I(1)	123.4(5)
O(1)–N(2)	1.389(8)	C(2)–C(1)–I(1)	125.9(5)
I(1′)–C(1′)	2.079(7)	N(2)–O(1)–N(1)	110.9(5)
C(2′)–N(2′)	1.300(9)	C(2)–N(2)–O(1)	105.5(5)
C(2′)–N(3′)	1.298(9)	N(3′)–C(2′)–N(2′)	124.6(7)
C(1′)–C(2′)	1.432(9)	N(2′)–C(2′)–C(1′)	107.8(6)
N(1′)–C(1′)	1.272(9)	N(3′)–C(2′)–C(1′)	127.6(7)
N(1′)–O(1′)	1.388(7)	C(1′)–N(1′)–O(1′)	104.0(5)
O(1′)–N(2′)	1.398(8)	N(1′)–C(1′)–C(2′)	111.8(6)
		N(1′)–C(1′)–I(1′)	123.6(5)
		C(2′)–C(1′)–I(1′)	124.6(5)
		N(1′)–O(1′)–N(2′)	111.5(5)
		C(2′)–N(2′)–O(1′)	104.9(6)

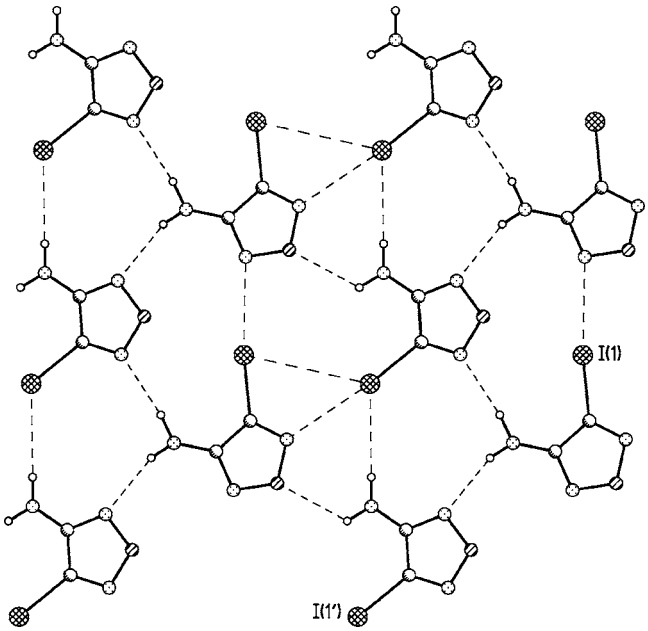


FIGURE 3 The packing scheme of **1d** in the crystal.

162.2 and 171.9°, respectively). For the second independent molecule, hydrogen atoms form only one strong H-bond with the iodine atom (H...I 2.93 Å, I...N 3.85 Å, N—H...I 179.2°) and one weak contact with oxygen atom (H...O 2.50 Å, O...N 3.06 Å, N—H...O 121.2°). Secondary interactions of iodine with nitrogen atoms of furazan in both independent molecules are almost equal (I...N 3.15 and 3.08 Å). Keeping in mind directed character of these contacts, that pointed out by C—I...N angles 174.8 and 173.3°, one can conclude that these contacts correspond to lone-pair electron transfer of the nitrogen atom to the antibonding C—I orbital.

The packing also contains I...I contacts: the layer plane contacts (between two independent molecules, I...I 4.08 Å, C—I...I 128.0°) and weaker interplanar ones (4.22 Å, C—I...I 107.4°). The values of C—I...I bind angles allow all I...I contacts to be suggested as forced.

The layer planes are situated close enough to each other (3.27 Å), that exhibit the presence of staking interactions between π-systems of furazan rings (Fig. 4).

During the search in the Cambridge Structural Database (CSD; Allen, 2002), several compounds containing furazan fragment were found. The analysis of their geometry has revealed that the values of bond lengths and angles in furazan ring are similar to those in **1d**. The minor deviations arised mainly from influence of substituents of various nature. Thus, mesomeric effect of substituent causes C=N bond elongation due to n-π (in the case of NH_2) and π-π (in the case of Ph) conjugation. This effect is strongest for phenyl substituent (C=N bond length equals ~1.35 Å), while in the case of amino

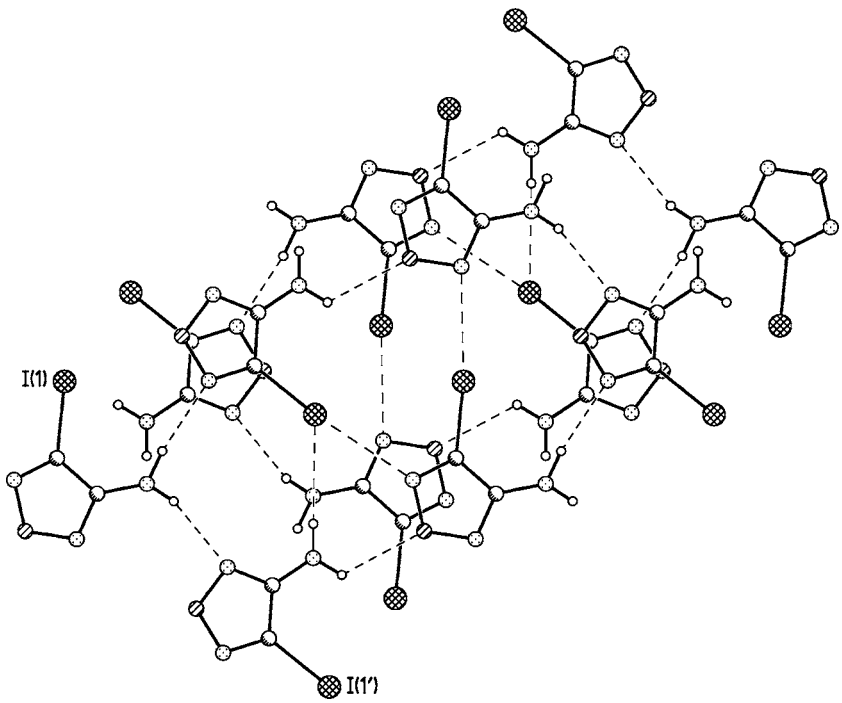


FIGURE 4 The formation of staking interactions in **1d.**

group there is almost no conjugation (C=N bond length is ~1.30 Å) because the corresponding distance between C and N at the methyl group is equal to ~1.29 Å. Despite of the analogous n-π mesomeric effects in **1d**, the C=N bond adjacent to the iodine atom in this molecule is shorter (~1.28 Å) than that at the amino group. This might be explained by the presence of negative inductive effect of iodine substitution that competes against the mesomeric one and its absence in other cases.

Also, it would be interesting to notice that the packing in the crystal of methylamine substituted furazan [21] is similar to that in **1d**, i.e., two independent molecules of the unit cell form planar layers stabilized by intermolecular contacts. However, the hydrogens of second independent molecule forms two strong H-bonds with oxygen and nitrogen atoms in the furazan rings of adjacent molecules (H...O 2.21 and H...N 2.20 Å, N...O 3.05 and N...N 3.08 Å, N—H...O 161.7 and N—H...N 170.2°) whereas second independent molecule of **1d** has only one strong N—H...I contact and weak N—H...O.

CONCLUSION

In summary, the originally developed method involving the use of $NaNO_2$-I_2 has proven to be effective in transformation of aminofurazans to iodofurazans. Simple reaction procedure combined with easy workup and generally moderate yields make for an attractive alternative to syntheses of iodo derivatives of other π-deficient (het)arenes.

EXPERIMENTAL SECTION

General Information

Unless otherwise stated, reactions were performed with magnetic stirring using dry, distilled solvents. Solvents for reactions were purified by standard procedures. All reagents used are commercially available. Melting points were determined with an open capillary and are uncorrected. Infrared spectra were determined on a Perkin-Elmer Model 577 spectrometer in KBr pellets or thin films. Mass-spectra were recorded on a Varian MAT-311A instrument. UV spectra were taken in MeOH on a Beckman DU-7 spectrophotometer. ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C spectra at 75 MHz on a Bruker AM-300 instrument. Chemical shifts were reported in δ values relative to the residual solvent peaks in ^{1}H and ^{13}C NMR ($CDCl_3$). All reactions were monitored by thin-layer chromatography (TLC) using Merck silica gel 60 F_{254} precoated aluminum plates. TLC was visualized with UV light (254 nm). Flash chromatography was performed with CH_2Cl_2/pentane solvent system using 0.040–0.060 mm silica gel (230–400 mesh) or silica gel 60 (200–400 mesh). All separations were carried out under above conditions.

X-ray Crystallography

Intensities of 5521 reflections were measured with a Smart 1000 CCD diffractometer (λ(MoKα) = 0.71072 Å, ω-scans with 0.3° step in ω 5 s per frame exposure, $2\theta < 60°$) and 1565 independent reflections ($R_{int} = 0.0337$) were used in further refinement. Crystallographic data for **1d**: at 170 K $C_2H_2IN_3O$ ($M = 210.97$) are monoclinic, space group $P2_1/m$; $a = 7.318(2)$ Å, $b = 6.548(1)$ Å, $c = 10.688(2)$ Å, $V = 511.5(2)$ Å^3, $Z = 8$ ($Z' = 2$), $d_{calc} = 2.740$ g cm^{-3}, μ(MoKα) = 6.136 mm^{-1}, $F(000) = 384$.

The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. Hydrogen atoms were located from the Fourier synthesis and refined in the isotropic approximation. The refinement converged to w$R2 = 0.0873$ and GOF = 1.076 for all independent reflections ($R1 = 0.0366$ was calculated against F for 1237 observed reflections with $I > 2\sigma(I)$). All calculations were performed using the SHELXTL PLUS 5.10 [22] on IBM PC AT. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Center (CCDC) as supplementary publication numbers 228976.

General Procedure for Preparation of Iodofurazans

To a slurry (or a solution) of an aminofurazan **2a–f** (10 mmol) and I_2 (20 mmol) in a mixture of MeCN/CH_2Cl_2 (1/1, 20 ml) was added solid $NaNO_2$ (20 mmol) by small portions at room temperature and stirring. After stirring for 2–3 h (until TLC analysis indicated complete consumption of starting material), a mixture of pentane/CH_2Cl_2 (2/3, 30 ml) was added and resulting mixture was washed with H_2O (100 ml), 0.1 N solution of $Na_2S_2O_3$ (2 × 10 ml), and H_2O (2 × 20 ml), sequentially. Organic solution was dried over $MgSO_4$ and passed through a short SiO_2 pad and evaporated to give product. These compounds **1a–f** can be additionally purified by flash chromatography or sublimation onto a Dry Ice cooled cold finger when heated to 35–55°C/1 mm.

*3-Methyl-4-iodofurazan (**1a**).* A light yellow solid: mp 26–27°C. ^{1}H NMR δ 2.38 (Me). MS (EI),

m/z: 210 [M^+], 180 [$M^+ - NO$], 83 [$M^+ - I$]. The substance corresponded in all respects with the compound described earlier [3].

*3-Ethyl-4-iodofurazan (***1b***).* A light yellow oil, mp −7 to −6°C. ^{1}H NMR ($CDCl_3$)δ: 1.37 (3H, Me), 2.74 (2H, CH_2). MS, *m/z*: 224 [M^+].

*3-Methoxy-4-iodofurazan (***1c***).* A light yellow solid: mp 27–27.5°C. IR (ν/cm^{-1}): 2948, 1580, 1476, 1450, 1420, 1384, 1204, 1124, 1000, 848, 712, 700, 664. ^{1}H NMR ($CDCl_3$) δ: 4.12 (OMe). MS, *m/z*: 226 [M^+].

*3-Amino-4-iodofurazan (***1d***).* A light yellow solid: mp 26–27°C. IR (ν/cm^{-1}): 3472, 3420, 3384, 3336, 3200, 1636, 1620, 1568, 1468, 1404, 1120, 972, 856, 716. ^{1}H NMR (DMSO-d_6) δ: 6.22 (NH_2). MS, *m/z*: 211 [M^+], 180 [$M^+ - NO$], 127 [I^+], 84 [$M^+ - I$], 54 [$M^+ - I - NO$].

*3-Bromo-4-iodofurazan (***1e***).* A light yellow oil, mp −11 to −9°C. IR (ν/cm^{-1}): 1616, 1488, 1380, 1308, 1280, 1035, 982, 916, 860, 832, 812. MS, *m/z*: 275 [M^+], 195 [$M^+ - Br$], 148 [$M^+ - I$], 127 [I^+]. Anal. Calcd for $C_2Br_1I_1N_2O_1$ (274.84): C 8.74, N 10.19. Found: C 8.77, N 10.15.

*3,4-Diiodofurazan (***1f***).* A light yellow solid: mp 64–65°C. IR (ν/cm^{-1}): 1616, 1436, 1276, 1252, 1016, 980, 868, 860. MS, *m/z*: 322 [M^+], 254 [I_2^+], 195 [$M^+ - I$], 165 [$M^+ - I - NO$], 127 [I^+]. Anal. Calcd for $C_2I_2N_2O_1$ (321.84): C 7.46, N 8.70, I 78.86. Found: C 7.42, N 8.66, I 78.81.

*3-Iodo-4-phenylfurazan (***1g***).* A light yellow solid: mp 107–108°C (dec). IR (ν/cm^{-1}): 2920–2875, 1580, 1540, 1488, 1448, 1408, 1352, 1164, 1004, 996, 980, 876, 840, 768, 716, 696. ^{1}H NMR δ 7.57 (3H), 7.89 (2H). MS, *m/z*: 272 [M^+], 145 [$M^+ - I$], 127 [I^+], 115 [$M^+ - I - NO$]. Anal. Calcd for $C_8H_5I_1N_2O_1$ (272.05): C 35.32, H 1.85, N 10.30, I 46.65. Found: C 35.30, H 1.89, N 10.25, I 46.69.

*3-Acetylamino-4-iodofurazan (***5***).* A mixture of amine **1d** (0.3 g, 1.4 mmol) and acetyl chloride (2 ml) was stirred at room temperature for 2 h. The precipitated crystals were filtered, washed with CCl_4 (3 × 5 ml), and dried in a vacuum oven at 40°C; yield was 0.35 g (90%), mp 150–152°C. A sample was recrystallized from CCl_4; mp 152–153°C. IR (ν/cm^{-1}): 3212, 3088, 3044, 2328, 1708, 1556, 1332, 1240, 1124, 860, 668, 596. ^{1}H NMR (DMSO-d_6) δ 2.12 (Me), 10.67 (NH). MS (EI), m/z: 253 [M^+], 211 [$M^+ - COMe$], 127 [I^+], 126 [$M^+ - I$]. Anal. Calcd for $C_4H_4I_1N_3O_2$ (253.00): C 18.99, H 1.59, N 16.61, I 50.16. Found: C 19.01, H 1.62, N 16.57, I 50.12.

*(3-Iodofurazan-4-yl)dichloroimine (***6***).* To a solution of amine **1d** (0.42 g, 2 mmol) in CCl_4 (10 ml) at room temperature, $AlCl_3$ (1.88 g, 0.014 mol) was added in a single portion with stirring under anhydrous conditions. The reaction mixture was vigorously stirred at 60–70°C for about 2.5 h, until the complete consumption of the starting amine (according to TLC). The mixture was cooled to room temperature and poured with stirring over 20 g of ice and water. The quenched mixture was extracted with CH_2Cl_2 (2 × 20 ml). The combined extracts were washed with cold water until neutral and dried with $MgSO_4$. The solution was passed through a short SiO_2 pad and evaporated to give product as clear liquid (0.36 g, 67%) that slowly crystallized, mp 29°C. MS, *m/z*: 295, 293, 291 [M^+]. Anal. Calcd for $C_3Cl_2I_1N_3O_1$ (291.86): C 12.35, N 14.40. Found: C 12.29, N 14.34.

*3-Iodo-4-(pyrrol-1-yl)furazan (***7***).* A solution of amine **1d** (0.42 g, 2 mmol) in AcOH (3 ml) was treated with 2,5-dimethoxytetrahydrofuran (0.29 g, 2.2 mmol). The mixture was heated to reflux for 1 h, cooled, and the solvent was evaporated in a rotary evaporator. The residue was taken up in CH_2Cl_2 (25 ml), washed with 5% aqueous K_2CO_3 (3 × 5 ml), water (5 × 3 ml), dried with $MgSO_4$, passed through a short SiO_2 pad and concentrated to give product as clear liquid (0.17 g, 32.5%). IR (ν/cm^{-1}): 2920, 2848, 1572, 1464, 1376, 1212, 1100, 1012, 908, 884, 728. ^{1}H NMR δ 6.49 (β), 7.48 (α). MS, *m/z*: 261 [M^+], 134 [$M^+ - I$], 127 [I^+], 104 [$M^+ - I - NO$]. Anal. Calcd for $C_6H_4I_1N_3O_1$ (261.02): C 27.61, H 1.54, N 16.10, I 48.62. Found: C 27.57, H 1.51, N 16.03, I 48.69.

*3-Azido-4-iodofurazan (***8***).* Amine **1d** (1.05 g, 5 mmol) was added to nitrosylsulfuric acid prepared by dissolving $NaNO_2$ (0.35 g, 5 mmol) in H_2SO_4 (4 ml) with efficient stirring in an ice bath. After 30 min the mixture was diluted with AcOH (5 ml) and a solution of NaN_3 (0.6 g, 10 mmol) in H_2O (4 ml) was added slowly from dropping funnel at such a rate that the temperature was kept between 0 and 5°C. After the end of the addition the mixture was stirred for 2 h at 15°C. It was diluted with water (50 ml) and extracted with CH_2Cl_2 (3 × 15 ml). The combined extract was washed with 5% aqueous K_2CO_3 (3 × 5 ml), water (2 × 7 ml), dried with $MgSO_4$, passed through a short SiO_2 pad, and concentrated. The residue was crystallized from CCl_4 to give product as colorless crystals (0.65 g, 65%); mp 92–92.6°C. IR (ν/cm^{-1}): 2324, 1636, 1620, 1568, 1468, 1120, 972, 856. ^{14}N

NMR ($CDCl_3$) δ: −145.9, −345.6 (N_3). Anal. Calcd for $C_2I_1N_5O_1$ (236.96): C 10.14, N 29.56. Found: C 10.17, N 29.50.

4,4′-Diiodoazofurazan (**9**). To a slurry of DBI (0.57 g, 2 mmol) in CH_2Cl_2 (35 ml) was added amine **1d** (0.21 g, 1 mmol) in one portion. After stirring for 1.5 h the mixture was passed through a short SiO_2 pad and concentrated. The residue was crystallized from hexane to give product as orange crystals (0.18 g, 85%); mp 158–159°C. IR (ν/cm^{-1}): 1616, 1576, 1560, 1540, 1504, 1456, 1404, 1352, 1124, 1020, 920, 800, 736. MS, *m/z*: 418 [M^+], 388 [M^+ − NO], 358 [M^+ − 2NO], 292 [M^+ − I], 261 [M^+ − NO − I], 127 [I^+]. Anal. Calcd for $C_4I_2N_6O_2$ (417.89): C 11.50, N 20.11, I 60.74. Found: C 11.51, N 20.06, I 60.77.

REFERENCES

[1] Sheremetev, A. B.; Makhova, N. N.; Friedrichsen, W. Adv Heterocycl Chem 2001, 78, 65–188.

[2] Birckenbach, L.; Sennewald, K. Liebigs Ann Chem 1931, 489, 7–31.

[3] Rakitin, O. A.; Zalesova, O. A.; Kulikov, A. S.; Makhova, N. N.; Godovikova, T. I.; Khmelnitskii, L. I. Izv Akad Nauk, Ser Khim 1993, 1949–1953 (in Russian) [Russian Chem Bull (English Translation) 1993, 42, 1865–1870].

[4] Melnikova, T. M.; Novikova, T. S.; Khmelnitskii, L. I.; Sheremetev, A. B. Mendeleev Commun 2001, 30–31.

[5] Sheremetev, A. B.; Aleksandrova, N. S.; Mantseva, E. V.; Dmitriev, D. E. Mendeleev Commun 2000, 67–69.

[6] (a) Tselinskii, I. V.; Melnikova, S. F.; Vergizov, S. N.; Frolova, G. M. Khim Geterotsikl Soedin 1981, 35–37 (in Russian) [Chem Heterocycl Compd (English Translation) 1981, 17, 27–29]; (b) Tselinskii, I. V.; Melnikova, S. F.; Vergizov, S. N. Khim Geterotsikl Soedin 1981, 321–324 (in Russian) [Chem Heterocycl Compd (English Translation) 1981, 17, 228–231].

[7] Godovikova, T. I.; Rakitin, O. A.; Khmelnitskii, L. I. Usp Khim 1983, 52, 777–786 (in Russian) [Russ Chem Rev (English Translation) 1983, 52, 440–445.

[8] (a) Smith, W. B.; Ho, O. C. J Org Chem 1990, 55, 2543–2546; (b) Cornforth, J.; Kuman, A.; Stuart, A. S. J Chem Soc, Perkin Trans 1, 1987, 859–866.

[9] (a) Nair, V.; Richardson, S. G. J Org Chem 1980, 45, 3969–3974; (b) Nair, V.; Richardson, S. G. Synthesis 1982, 670–672; (c) Nair, V.; Young, D. A.; DeSilvia, R. J Org Chem 1987, 52, 1344–1347; (d) Tanji, K.; Kato, H.; Higashino, T. Chem Pharm Bull 1991, 39, 2793–2796.

[10] Coad, E. C.; Liu, H.; Rasmussen, P. G. Tetrahedron 1999, 55, 2811–2826.

[11] Paudler, W. W.; Shin, H. G. J Org Chem 1968, 33, 1638.

[12] Sheremetev, A. B.; Aleksandrova, N. S.; Yudin, I. L. Mendeleev Commun 2003, 1, 30–31.

[13] Sheremetev, A. B.; Konkina, S. M.; Yudin, I. L.; Dmitriev, D. E.; Averkiev, B. B.; Antipin, M. Yu. Izv Acad Nauk, Ser Khim 2003, 1337–1342 (in Russian); Russ Chem Bull, Int Ed (English Translation), 2003, 52, 1413–1418.

[14] Sheremetev, A. B.; Shatunova, E. V.; Averkiev, B. B.; Dmitriev, D. E.; Petukhov, V. A.; Antipin, M. Yu. Heteroat Chem 2004, 15, 131–145.

[15] Paton, R. M. In Comprehensive Heterocyclic Chemistry; Katritzky, A. R.; Rees, C. W.; Scriven, E. F. V. (Eds.); Pergamon Press: Oxford, 1996; Vol. 4, pp. 229–265.

[16] Novikova, T. S.; Melnikova, T. M.; Kharitonova, O. V.; Kulagina, V. O.; Aleksandrova, N. S.; Sheremetev, A. B.; Pivina, T. S.; Khmelnitskii, L. I.; Novikov, S. S. Mendeleev Commun 1994, 138–140.

[17] Ewing, D. F. Org Magn Reson 1979, 12, 499–524.

[18] Lynch, B. M. Can J Chem 1977, 55, 541–547.

[19] Dmitriev, D. E. Strelenko, Yu. A.; Sheremetev, A. B. Izv Acad Nauk, Ser Khim 2002, 2, 277–282; Russ Chem Bull, Int Ed (English Translation), 2002, 51, 290–296.

[20] Sheremetev, A. B.; Andrianov, V. A.; Mantseva, E. V.; Shatunova, E. V.; Aleksandrova, N. S.; Kulagina, V. O.; Melnikova, T. M.; Yudin, I. L.; Dmitriev, D. E.; Averkiev, B. B.; Antipin, M. Yu. Izv Acad Nauk, Ser Khim (in press); Russ Chem Bull, Int Ed (English Translation), (in press).

[21] Viterbo, D.; Serafino, A. Acta Crystallogr, Sect B: Struct Crystallogr Cryst Chem 1978, 34, 3444–3446.

[22] Sheldrick G. M. SHELXTL v. 5.10, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA, 1998a.