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Thermally induced rearrangement of the arylhydrazones of furoxan-3-yl carbonyl compounds

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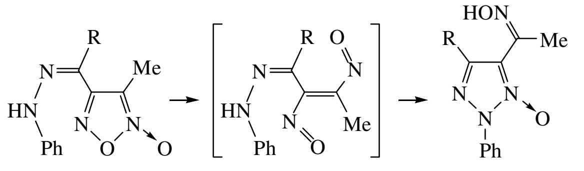
A thermally induced rearrangement of arylhydrazones 5 of furoxan-3-yl carbonyl compounds into 2-aryl-5-[(hydroximino)(aryl)-methyl]-2*H*-1,2,3-triazole 1-oxides 6 has been found for the first time; the crystal packing of compound 6a has been studied by X-ray diffraction analysis.

Previously, we found new rearrangements in the series of non-condensed furoxan derivatives.[1–7] Rearrangements of this kind in furoxan derivatives were published only as a few examples.[8–10] The driving force of furoxan derivative rearrangements into other heterocycles is a nucleophilic attack of a substituent at the 4-position of the furoxan ring on the N(5) atom followed by O(1)–N(5) bond cleavage and formation of other azole derivatives. The other azole derivatives participate in azole–azole rearrangements by a similar scheme.[11,12] However, as distinct from other azoles, the furoxan ring is capable of a thermal O(1)–N(2) bond cleavage with the formation of short-lived dinitrosoethylene intermediate **A**. Using this property of the furoxan ring, we were the first to carry out thermally induced rearrangements of 3,3′-azo-4,4′-bis(acetylamino)furoxans[4] and 3-arylazo-4-(3-ethoxycarbonylureido)furoxans[6] into corresponding 4-amino-2-furoxanyl(aryl)-5-nitro-2*H*-1,2,3-triazoles, as well as of 4-acetyl(benzoyl)-3-methylfuroxan phenylhydrazones **1** into 5-acetyl-4-methyl(phenyl)-2-phenyl-2*H*-1,2,3-triazole 1-oxide oximes **2**[1] (Scheme 1). According to the mechanism proposed,[1,4,6] a nitroso group in intermediate **A** is attacked by the adjacent phenylhydrazone substituent at the 4-position of initial furoxan **1** to form triazole oxides **2**. The last reaction was the first example



R = Me, Ph

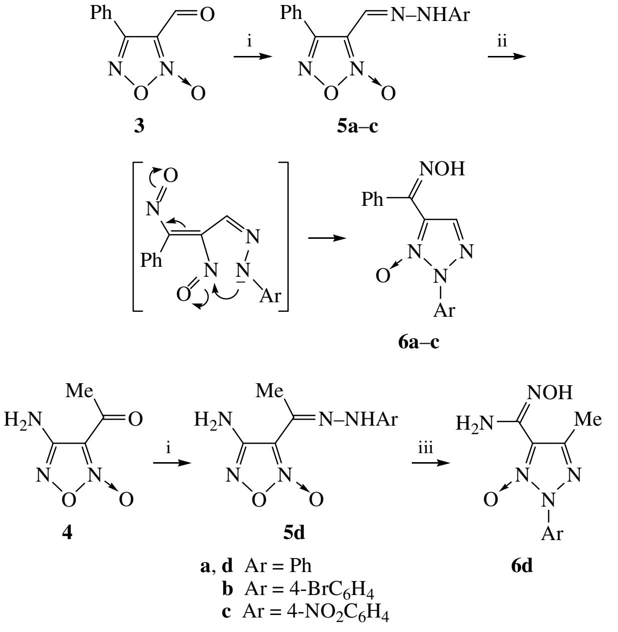
Scheme 1

of a trapping of the dinitrosoethylene intermediate generated at the thermal ring-opening of non-condensed furoxan derivative.

Until now, all furoxan derivatives, which underwent rearrangements, contained a necessary substituent at the 4-position of the ring since the N-oxide oxygen atom adjacent to the C(3) carbon atom hindered the nucleophilic attack of the substituent. We assumed that, given the actual formation of intermediate **A** under the thermal rearrangement conditions, appropriate derivatives of furoxan-3-yl carbonyl compounds could also enter the rearrangement. To test this assumption, we studied the possibility of the thermal rearrangement of arylhydrazones of furoxan-3-yl carbonyl compounds.

4-Phenylfuroxan-3-carboxaldehyde[13] **3** and 3-acetyl-4-aminofuroxan[14] **4** were used as initial carbonyl compounds. Arylhydrazones **5a–d** were synthesised according to a standard procedure by refluxing compounds **3** and **4** with corresponding arylhydrazine hydrochloride in isopropanol. The possibility of rearranging hydrazones **5a–d** into 1,2,3-triazole 1-oxide derivatives **6** was investigated by their refluxing in solvents (methanol, toluene and xylene) and in the presence of different additives. It was found that hydrazones **5a–d** were really capable of entering the sought thermally induced rearrangement, the rearrangement conditions for compound **5a–c** being milder than those for compound **5d**. Arylhydrazones **5a–c** were transformed into 2-aryl-5-[(hydroximino)(aryl)methyl]-2*H*-1,2,3-triazole 1-oxides **6a–c** in 68–95% yields by refluxing in methanol in the presence of potassium hydroxide in an equimolar amount followed by acidification of the reaction mixture. The involvement of phenylhydrazone **5d** in the rearrangement was only achieved through its refluxing in *o*-xylene with the formation of corresponding 1,2,3-triazole 1-oxide **6d** in 35% yield (Scheme 2).

The structure of the synthesised compounds was established by the overall data of the elemental analysis, spectral characteristics† and X-ray diffraction study for compound **6a**.‡ According to the X-ray diffraction study of a crystal of **6a**, the bond lengths in 1,2,3-triazole are characterised by slight asymmetry typical of heterocycles of this type (Figure 1).[2,15]



a, **d** Ar = Ph
b Ar = 4-BrC_6H_4
c Ar = 4-$NO_2C_6H_4$

Scheme 2 *Reagents and conditions*: i, $ArNHNH_2 \cdot HCl$, Pr^iOH, refluxing for 0.5 h; ii, dry MeOH, KOH (1 mol), refluxing for 3 h, then $AcOH/H_2O$; iii, *o*-xylene, refluxing for 3 h.

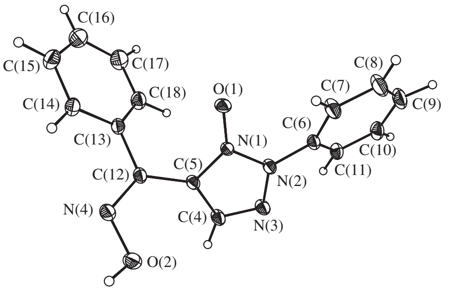


Figure 1 General view of compound **6a** showing the atom labeling and thermal ellipsoids at a 50% probability level. The bond lengths (Å) and angles (°): N(1)–O(1) 1.281(1), N(1)–N(2) 1.367(1), N(2)–N(3) 1.344(1), N(3)–C(4) 1.332(1), N(1)–C(5) 1.357(1), C(12)–N(4) 1.296(1), N(4)–O(2) 1.397(1), O(1)–N(1)–N(2) 123.2(1), N(2)–N(1)–C(5) 107.1(1), N(1)–N(2)–N(3) 111.3(1), N(2)–N(3)–C(4) 105.3(1), C(12)–N(4)–O(2) 112.8(1).

Indeed, the N(2)–N(3) and N(3)–C(4) bonds are slightly shorter than N(2)–N(1) and N(1)–C(5) ones. The dihedral angle

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† IR spectra were measured on a UR-20 spectrometer; ^1H and ^{13}C NMR spectra were recorded on Bruker WM-250 (250 MHz) and Bruker AM-300 (75.5 MHz) spectrometers, respectively ($CDCl_3$ was used as an internal standard). Mass spectra were measured on a Finnigan MAT INCOS-50 instrument. TLC was carried out on Silufol UV-254 plates. New compounds were separated on Kieselgel 60 F_{254} (Merck). Melting points were measured on a Gallenkamp instrument (Sanyo).

4-Phenylfuroxan-3-carboxaldehyde phenylhydrazone **5a**: yield 76%, mp 144–145 °C. ^1H NMR ([$^2H_6$]DMSO) δ: 6.81, 7.19 (2m, 5H, PhN), 7.63, 7.85 (2m, 6H, PhC, CH), 11.09 (s, 1H, NH). MS, *m/z*: 280 (M^+).

4-Phenylfuroxan-3-carboxaldehyde 4-bromophenylhydrazone **5b**: yield 68%, mp 151–152 °C. ^1H NMR ([$^2H_6$]DMSO) δ: 6.72, 7.35 (AA′BB′, 4H, Ar, ^3J 7.4 Hz), 7.65, 7.85 (2m, 6H, Ph, CH), 11.18 (s, 1H, NH). MS, *m/z*: 360 (M^+, ^{81}Br), 358 (M^+, ^{79}Br).

4-Phenylfuroxan-3-carboxaldehyde 4-nitrophenylhydrazone **5c**: yield 56%, mp 169–170 °C. ^1H NMR ([$^2H_6$]DMSO) δ: 6.89, 8.11 (AA′BB′, 4H, Ar, ^3J 7.8 Hz), 7.72, 7.80 (2m, 6H, Ph, CH), 11.76 (s, 1H, NH). MS, *m/z*: 325 (M^+).

3-Acetyl-4-aminofuroxan phenylhydrazone **5d**: yield 63%, mp 164–165 °C, R_f 0.68 (eluent: $CHCl_3$–EtOAc, 5:1). ^1H NMR ([$^2H_6$]DMSO) δ: 2.35 (s, 3H, Me), 6.49 (s, 2H, NH_2), 6.85–7.28 (m, 5H, Ph), 9.85 (s, 1H, NH). ^{13}C NMR ([$^2H_6$]DMSO) δ: 11.4 (Me), 108.9 [C(3) furoxan ring], 113.2, 120.5, 129.1, 130.9 (Ph), 144.3 [C(4) furoxan ring], 156.1 (C=NNH). IR (ν/cm^{-1}): 3448, 3336, 3296, 1612, 1564, 1476, 1308, 1256, 1132, 1072, 952, 752, 648. MS, *m/z*: 233 (M^+).

*5-[(Hydroxyimino)(phenyl)methyl]-2-phenyl-2*H*-1,2,3-triazole 1-oxide* **6a**: yield 68%, mp 175–176 °C, R_f 0.43 (eluent: $CHCl_3$–EtOAc, 7:1). ^1H NMR ([$^2H_6$]DMSO) δ: 7.41–7.92 (m, 10H, 2Ph), 8.39 (s, 1H, CH), 12.32 (s, 1H, OH). ^{13}C NMR ([$^2H_6$]DMSO) δ: 120.1, 123.4, 126.4, 128.5, 129.2, 129.4, 129.5, 132.9 (2Ph), 134.4 [C(5) triazole ring], 135.1 (C=NOH), 142.7 [C(4) triazole ring]. IR (ν/cm^{-1}): 3156, 3064, 1592, 1500, 1420, 1392, 1328, 1008, 956, 928, 784, 756, 692. MS, *m/z*: 280 (M^+).

*2-(4-Bromophenyl)-5-[(hydroxyimino)(phenyl)methyl]-2*H*-1,2,3-triazole 1-oxide* **6b**: yield 96%, mp 189–190 °C, R_f 0.60 (eluent: $CHCl_3$–EtOAc, 7:1). ^1H NMR ([$^2H_6$]DMSO) δ: 7.41–7.95 (m, 9H, 2Ar), 8.39 (s, 1H, CH), 12.32 (s, 1H, OH). ^{13}C NMR ([$^2H_6$]DMSO) δ: 120.2, 122.3, 125.1, 126.4, 128.5, 129.4, 132.2, 132.8 (Ar), 133.6 [C(5) triazole ring], 135.5 (C=NOH), 142.6 [C(4) triazole ring]. IR (ν/cm^{-1}): 3275, 3144, 1488, 1448, 1400, 1348, 1288, 1096, 1020, 932, 828, 784, 692. MS, *m/z*: 360 (M^+, ^{81}Br), 358 (M^+, ^{79}Br).

*2-(4-Nitrophenyl)-5-[(hydroxyimino)(phenyl)methyl]-2*H*-1,2,3-triazole 1-oxide* **6c**: yield 91%, mp 209–210 °C, R_f 0.54 (eluent: $CHCl_3$–EtOAc, 7:1). ^1H NMR ([$^2H_6$]DMSO) δ: 7.35–7.62 (m, 5H, Ph), 8.25, 8.49 (AA′BB′, 4H, Ar, ^3J 7.7 Hz), 8.40 (s, 1H, CH), 12.32 (s, 1H, OH). ^{13}C NMR ([$^2H_6$]DMSO) δ: 120.8, 122.7, 124.7, 126.4, 128.5, 129.4, 132.6, 136.4 (Ar), 138.9 [C(5) triazole ring], 142.4 (C=NOH), 146.4 [C(4) triazole ring]. IR (ν/cm^{-1}): 3275, 3112, 1596, 1528, 1404, 1348, 1016, 932, 856, 784, 692. MS, *m/z*: 325 (M^+).

*5-[Amino(hydroxyimino)methyl]-4-methyl-2-phenyl-2*H*-1,2,3-triazole 1-oxide* **6d**: yield 35%, mp 198–199 °C, R_f 0.30 (eluent: $CHCl_3$–EtOAc, 5:1). ^1H NMR ([$^2H_6$]DMSO) δ: 2.40 (s, 3H, Me), 6.35 (s, 2H, NH_2), 7.53–7.81 (m, 5H, Ph), 11.50 (s, 1H, OH). ^{13}C NMR ([$^2H_6$]DMSO) δ: 14.1 (Me), 119.8, 123.7, 129.1, 129.3 (Ph), 134.1 [C(5) triazole ring], 141.4 (C=NOH), 143.2 [C(4) triazole ring]. IR (ν/cm^{-1}): 3468, 3336, 3068, 1648, 1580, 1496, 1444, 1324, 1084, 944, 704, 660. MS, *m/z*: 233 (M^+).

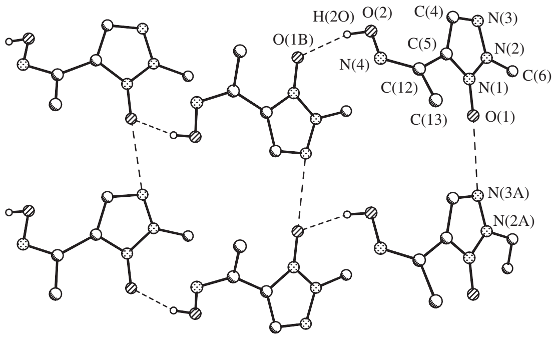

Figure 2 Fragment of a corrugated layer in the structure of **6a**. The phenyl rings and H atoms except for OH groups are omitted for clarity.

between the triazole and phenyl C(6)–C(11) rings is 32.1° and the O(2)–N(4)–C(12)–C(13) and N(1)–C(5)–C(12)–C(13) torsion angles are equal to 178.3 and 42.7°, respectively.

Note that **6a** crystallises in non-centrosymmetric space group *Pn* and thus can be interesting as a nonlinear optical material. In the crystal of **6a**, the molecules are assembled into infinite corrugated layers by the O(2)–H(2O)···O(1) H-bond of moderate strength [O···O distance is 2.709(1) Å] and by the shortened O(1)···N(3) [2.853(1) Å] non-bonded contact (Figure 2). The latter is characterised by considerable directionality and N(1)–O(1)···N(3A) and O(1)···N(3A)–N(2A) angles equal to 171.8 and 169.8°, respectively. Such geometrical parameters of the contact can be regarded as an indication of the stereoelectronic interaction either of the O(1) electron lone pair (Lp) with the σ*[N(2A)–N(3A)] orbital or, alternatively, of Lp of the N(3A) atom with σ*[N(1)–O(1)].

In terms of the formally semipolar nature of the O(1)–N(1) bond, it is impossible to predict the number and mutual disposition of Lp of the O(1) atom from the geometry viewpoint.

Thus, to achieve a deeper insight into the nature of the O(1)···N(3A) contact, we performed a topological analysis of electron density $\rho(r)$ in the crystal of **6a** within the framework of Bader's Atom in Molecule (AIM) theory.[16]

The analysis of atomic charges obtained by integrating $\rho(r)$ over atomic basins (Ω) (subspaces surrounded by zero-flux surfaces)[16] in the crystal of **6a** has revealed that corresponding parameters for O(1), N(1), N(2) and N(3) are –0.25, –0.19, –0.43 and –0.46 e, respectively. These values indicate that the semipolar character of the O(1)–N(1) bond is not observed in **6a** and that both O(1) and N(3) atoms involved in the interaction have negative charges.

Note that non-bonded interactions formed by atoms with closed shells, in general, can be described in the light of the peak-hole formalism.[17] Surprisingly, the analysis of deformation electron density (DED) maps in the area of the said contact has shown that the lone pairs of O(1) and N(3A) atoms are directed to each other (Figure 3).

As a result of the topological analysis of the $-\nabla^2\rho(r)$ function, two maxima [critical points (3, –3)] attributed to the Lp according to the Lewis model[16] have been located around O(1). Thus, the second one is oriented toward H(4A), probably, being involved in the C–H···O [H···O distance is 1.77(2) Å] intermolecular contact (Figure 3). Indeed, a search of the bond critical points (3, –1) in their area has revealed that the O(1) atom interacts with both N(3A) and H(4A) atoms. However, the energy of these contacts (E_{cont}) estimated on the basis of the correlation proposed by Lecomte[18] is 1.97 and 2.2 kcal mol^{-1} for O(1)···N(3A) and O(1)···H(4A), respectively. For comparison, the E_{cont} value in the case of O(2)–H(2O)···O(1B) H-bond is 8.1 kcal mol^{-1}.

Therefore, the described peak–peak O(1)···N(3A) interaction in **6a** may be considered as forced in nature and is, probably, with the account of negative charges of O(1) and N(3) atoms, governed by dispersive forces.

Taking into account the relatively high melting point of **6a**, as well as its asymmetric crystal structure, we estimated the second order nonlinear optical properties of **6a** based on molecular hyperpolarizability calculated within the PM3 approximation. Crystal susceptibility estimated in terms of the oriented gas model is comparable to corresponding theoretical values of well-known *meta*-substituted nitrobenzenes (R = Cl, Br or NH$_2$), which were estimated within the same level of approximation.[19] Crystal susceptibility tensor coefficients of **6a** are $d_{xxx} = 0.25$, $d_{xyy} = 1.72$, $d_{xzz} = 0.10$, $d_{xxz} = 1.60$, $d_{yyz} = 2.67$ and $d_{zzz} = 0.99\times10^{-9}$ esu.

Thus, we found for the first time that not only derivatives of furoxan-4-yl carbonyl compounds but also analogous derivatives of furoxan-3-yl carbonyl compounds are able to enter the thermally induced furoxan–azole rearrangement. The reaction once more experimentally supported a possibility for the trapping of the dinitrosoethylene intermediate generated by thermal ring opening of a furoxan ring. The X-ray study of compound **6a** identified the specific features of its crystal packing, which was analysed within the topological analysis of electron density in a crystal.

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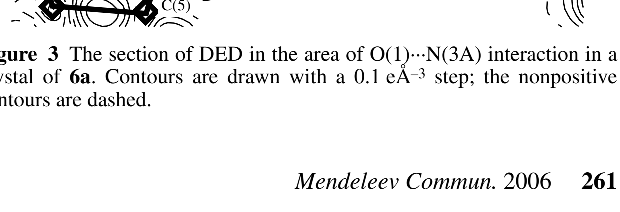

Figure 3 The section of DED in the area of O(1)···N(3A) interaction in a crystal of **6a**. Contours are drawn with a 0.1 eÅ^{-3} step; the nonpositive contours are dashed.

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‡ *Crystallographic data.* Crystals of **6a** ($C_{15}H_{12}N_4O_2$, $M = 280.29$) are monoclinic, space group *Pn*, at 178 K: $a = 9.940(1)$ Å, $b = 6.210(1)$ and $c = 11.431(1)$ Å, $\beta = 110.81(1)°$, $V = 659.52(14)$ Å^3, $Z = 2$ ($Z' = 1$), $d_{\text{calc}} = 1.411$ g cm^{-3}, μ(MoKα) = 0.98 cm^{-1}, $F(000) = 292$. Intensities of 8728 reflections were measured with a Syntex $P2_1$ diffractometer [λ(MoKα) = 0.71072 Å, $\theta/2\theta$ scans, $2\theta < 100°$] and 5898 independent reflections [$R_{\text{int}} = 0.0452$] were used in the further refinement. The structure was solved by a 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 of the electron density and refined in the isotropic approximation. For **6a**, the refinement converged to $wR_2 = 0.087$ and GOF = 0.985 for all independent reflections [$R_1 = 0.0373$ was calculated against F for 3153 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0.

The multipole refinement was carried out within the Hansen-Coppens formalism[20(*a*)] using the XD program package[20(*b*)] with the core and valence electron density derived from wave functions fitted to a relativistic Dirac–Fock solution. Before the refinement, C–H and O–H bond distances were normalised to the values 1.08 and 0.98 Å, respectively. The level of multipole expansion was octopole for carbon, nitrogen and oxygen atoms and dipole for hydrogens. The multipole occupancies of all the nonhydrogen atoms except for O(1), O(2), N(4) and C(12) were refined with the *m* symmetry restrains, respectively.[20(*c*)] The refinement was carried out against F and converged to $R = 0.0251$, $wR = 0.0246$ and GOF = 0.7382 for 3132 merged reflections with $I > 3\sigma(I)$. Almost all bonded pairs of atoms satisfy the Hirshfeld rigid-bond criteria[20(*d*)] (difference of the mean square displacement amplitudes along the bond only for several atomic pairs were insignificantly larger than 10×10^{-4} Å^2). The residual electron density was no more that 0.11 eÅ^{-3}. Analysis of topology of the $\rho(r)$ function was carried out using the WINXPRO program package.[21]

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 619879. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2006.

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