Synthesis, structure, and properties of *N*-(nitramino)phthalimide

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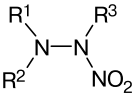
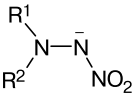
N-(Nitramino)phthalimide $R_2N—NHNO_2$ (R_2NH is phthalimide) was synthesized by nitration of *N*-aminophthalimide with nitronium tetrafluoroborate. The structure of this compound was established by X-ray diffraction and confirmed by ^1H, ^{13}C, and ^{14}N NMR spectroscopy. The methylation of this compound with diazomethane affords a mixture of *N*-methyl ($R_2N—NMeNO_2$) and *O*-methyl ($R_2N—N=N(O)OMe$) isomers. The latter compound contains the previously unknown high-nitrogen-oxygen fragment. The thermal decomposition of *N*-(nitramino)phthalimide *in vacuo* at 80—100 °C gives 2*H*-3,1-benzoxazine-2,4(1*H*)-dione (isatoic anhydride) as the major product.

Key words: primary nitramines, nitrohydrazines, diazomethane, nitronium tetrafluoroborate, nitration, thermolysis, X-ray diffraction study, NMR.

N-Nitrohydrazines **1** belong to high-nitrogen systems with a chain consisting of three nitrogen atoms.[1] A series of compounds containing the alkyl,[2] trifluoromethyl,[3,4] aryl,[5] acyl,[2,5] or alkoxycarbonyl groups[2] as the substituents R^1, R^2, and R^3 were synthesized. In addition, the synthesis of three *N*-nitrohydrazine salts **2**, where R^1 and R^2 are Me and Ac, Me and CO_2Me, or Me and CO_2Et, was documented. These salts are stable in the solid state under standard conditions; however, they rather rapidly decomposed in protic solvents,[2] due to which the corresponding nitrohydrazines **3** were not isolated.



1



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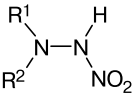
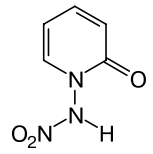
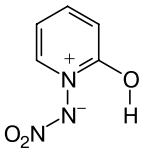


3

It should be noted that rather stable *N*-nitramino-2-pyridone **4a** (m.p. 120 °C) was synthesized. Structure **4a** containing the proton at the nitrogen atom rather than tautomeric form **4b** containing the proton at the oxygen atom was confirmed by the ^1H NMR spectra in DMSO-d_6[6].



4a



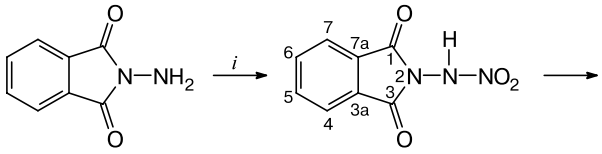
4b

The aim of the present study was to synthesize nitrohydrazine **3** containing electron-withdrawing groups as both substituents, R^1 and R^2. *N*-Aminophthalimide was chosen as a model compound.

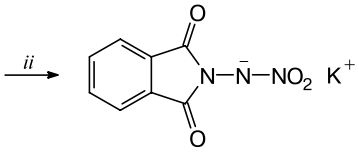
Results and Discussion

N-Aminophthalimide was nitrated with nitronium tetrafluoroborate in acetonitrile at −30 °C → 0 °C. To achieve the complete conversion of the starting compound, a small excess of the nitrating agent was used. *N*-(Nitramino)phthalimide **5** was prepared in 82% yield (Scheme 1).

Scheme 1



5



6

i. NO_2BF_4, MeCN, −30 °C → 0 °C, 82%; *ii*. KOH, MeOH, 77%.

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This compound is rather stable (remains virtually unchanged during storage at room temperature for two weeks) and melts with decomposition at 82—84 °C accompanied by gas evolution.

The structure of compound **5** was established by X-ray diffraction (see below). This compound can be considered as nitrohydrazine containing two electron-withdrawing substituents. At the same time, it is convenient to compare the properties of **5** with those of primary nitramines.

The treatment of compound **5** with a methanolic solution of KOH affords potassium salt **6** (see Scheme 1) as colorless needle-like crystals. These crystals undergo melting with decomposition at 268—286 °C. It should be noted that the thermal stability of salt **6** is substantially higher than that of potassium salts of nitrohydrazines **2** described earlier.[2]

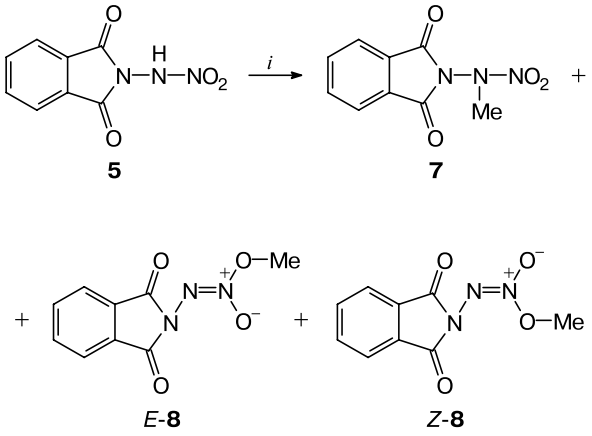
The structure of compound **5** was confirmed by NMR spectroscopy. The ^{1}H NMR spectrum in $CDCl_3$ shows a broad singlet for the NH proton at δ 9.94. In the ^{14}N NMR spectra, the chemical shift of the N atom of the nitro group substantially depends on the nature of the solvent. An increase in the solvent polarity leads to the downfield shift of the signal from −31 (in $CDCl_3$) to −12 ppm (in D_2O) (Table 1). Apparently, this is associated with an increase in the degree of dissociation of compound **5**. This suggestion is supported by the fact that the signal in the spectrum of K salt **6** (in D_2O) is shifted to even lower field (to −6 ppm). It should be noted that the chemical shift of the nitro group of compound **5** in $CDCl_3$ is similar to that of *N*-methyl derivative **7** (δ −28) in the same solvent and differs substantially from that of *O*-methyl derivative **8** (δ −40), the signal of the latter compound being substantially broadened. The same tendency is observed in the series of nitramines. For example,[7] the chemical shifts of the corresponding N atom in $Me_2CHNHNO_2$ and $Me_2CHN{=}N(O)OMe$ are −26 and −57 ppm, respectively, the latter signal being also substantially broadened.

Methylation of *N*-(nitramino)phthalimide 5. *N*-Nitro compound **5**, like primary nitramines,[8] reacts with diazomethane in an ethereal solution (Scheme 2) to give a mixture of *N*- and *O*-methyl derivatives **7** and **8** in a ratio of 1.7 : 1 (^{1}H NMR spectroscopic data). *O*-Methyl compound **8** was obtained as a mixture of two stereoisomers in a ratio of 4 : 1. It should be noted that this compound contains the previously unknown high-nitrogen-oxygen fragment.

Table 1. ^{14}N NMR spectra (δ, $\Delta\nu_{1/2}$/Hz) of *N*-(nitramino)phthalimide **5**, its K salt **6**, *N*-methyl derivative **7**, and *O*-methyl derivative **8**

Compound	Solven	δ ($\Delta\nu_{1/2}$/Hz)
5	$CDCl_3$	−31 (35)
5	Acetone-d_6	−27 (35)
5	D_2O	−12 (70)
6	D_2O	−6.0 (70)
7	$CDCl_3$	−28 (30)
8	$CDCl_3$	−40 (200)

Scheme 2



i. CH_2N_2, Et_2O, 20 °C, 99%

A mixture of isomers of **7** and **8** was separated by preparative TLC. Compound **7** melts at 85—87 °C without decomposition; compound **8** (a mixture of the *E* and *Z* isomers), at 125—140 °C with decomposition. The *E* and *Z* isomers can be separated by TLC in an EtOAc—hexane mixture (1 : 10) although the difference in their retention factors (R_f) is very small.

In the ^{1}H and ^{13}C NMR spectra, the signals of the methyl groups of *N*-methyl isomer **7** (δ_H 3.85, δ_C 42.9) and *O*-methyl isomers of **8** are substantially different. The signals of stereoisomers *E*-**8** and *Z*-**8** differ only slightly. Based on a comparison of the known ^{1}H (see Ref. 9) and ^{13}C (see Ref. 7) NMR data for the *E* and *Z* isomers of the *O*-methyl derivatives of primary nitramines with the data for compounds **8**, the *E* and *Z* configurations can be assigned with confidence to the major and minor isomers, respectively. For isomer *E*-**8**, δ_H 4.19 and δ_C 58.9; for isomer *Z*-**8**, the signals are shifted upfield (δ_H = 4.05, δ_C = 58.3), as in the case of the *O*-methyl derivatives of primary nitramines.

The mass spectrum (EI, 70 eV) of compound **7** does not show a molecular ion peak. This compound is characterized by the peak $[M - NO_2]^+$. The mass spectrum of a mixture of isomers *E*-**8** and *Z*-**8** has a molecular ion peak.

The presence of the nitro group in compound **5** and its *N*-methyl derivative **7** is confirmed by the IR spectra (in KBr; ν 1384 and 1628 cm^{-1} for **5** and 1384 and 1568 cm^{-1} for **7**).

Thermal stability. To compare the thermal stability of *N*- and *O*-methyl-substituted compounds **7** and **8**, these compounds were heated in tetrachloroethylene, after which their ^{1}H NMR spectra were recorded. Upon heating at 110 °C for 15 min, the degree of decomposition was 5 and 40% for isomers **7** and *Z*-**8**, respectively. The amount of isomer *E*-**8** remains unchanged. Upon further heating at 120 °C for 30 min, the degree of decomposition of isomer **7** was 33%; of compound *E*-**8**, 15%. Isomer *Z*-**8** virtually completely decomposed during this period of time.

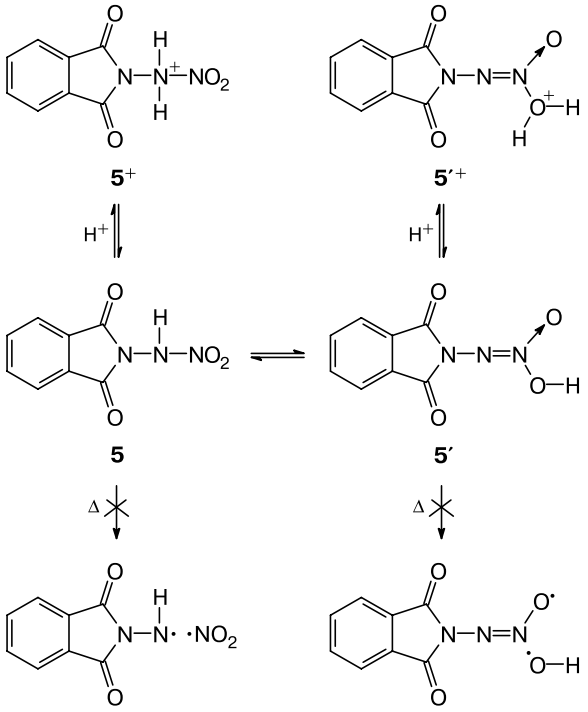
Therefore, *O*-methyl derivative *E*-**8** is thermally more stable than *N*-methyl derivative **7**. Earlier, it has been already noted that the *E* isomers are thermally more stable than the *Z* isomers in the series of *O*-methyl ethers of primary nitramines.[10]

Most likely, the decomposition of *N*-methyl-substituted compound **7**, by analogy with that of secondary nitramines,[11,12] starts with the radical cleavage of the N—NO_2 bond. It is also cannot be excluded that the decomposition of *O*-methyl compound **8**, by analogy with that of *O*-alkyl derivatives of primary nitramines,[13] starts with the radical cleavage of the N—OMe bond. The fact that *N*-(nitramino)phthalimide **5** is thermodynamically substantially less stable than compounds **7** and **8** indicates that there are, apparently, easier decomposition pathways for compound **5** compared to the radical cleavage of the N—NO_2 and N—OH bonds (Scheme 3). Apparently, this is associated with the presence of the N—H proton in molecule **5**.

Most probably, the decomposition of *N*-(nitramino)phthalimide **5**, like the thermal decomposition of primary nitramines in the condensed phase,[11,13] is accompanied by autoprotolysis. The protonation can proceed at both the N atom to form cation $\mathbf{5}^+$ and the O atom to form cation $\mathbf{5}'^+$ (see Scheme 3). Isomer **5′** is thermodynamically less stable* than isomer **5**. However, it can be formed upon heating. Apparently, both cations can initiate their own reaction chains. In the present study, we discuss only some features of these processes.

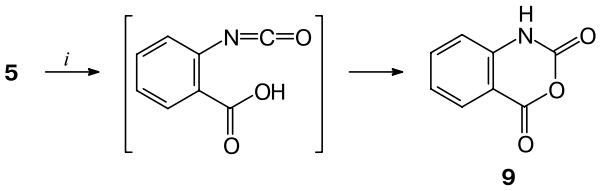
Heating of compound **5** under solvent-free conditions is accompanied by the release of an NO_2 brown gas. Nitrogen oxides can nitrosate nitramine **5** at the N—H bond. To eliminate the influence of NO_2, thermal decomposition of compound **5** was performed *in vacuo* with continuous removal of nitrogen oxides. In this case, the reaction performed at 80 → 100 °C gives isatoic anhydride **9** as the major product (Scheme 4) (*cf.* Ref. 14). The structure of **9** was unambiguously confirmed by IR and ^{1}H NMR spectroscopic data and the mass spectrum,

Scheme 3



which are completely identical to the data published in the literature[15,16] and are consistent with the ^{13}C NMR spectrum.

Scheme 4



i. 80—100 °C, 5 min, 42%

The available experimental data are insufficient to suggest the mechanism of formation of isatoic anhydride. Presumably, the reaction involves the Curtius rearrangement as one of the steps.

X-ray diffraction study of *N*-(nitramino)phthalimide 5. The X-ray molecular structure of **5** is shown in Fig. 1. The crystal structures of uncharged nitrohydrazines remain unknown. Data on the structures of the simplest nitrohydrazines in the isolated state were obtained by high-level quantum chemical calculations (G2, G3, and CBS-QB3).[17] The bond lengths and bond angles in the phthalimide fragment of **5** are virtually identical to the corresponding parameters in unsubstituted *N*-aminophthalimide,[18] except for the N(2)—C(1) and N(2)—C(3)

* Model methylisonitramine MeN=NOOH is thermodynamically less stable than isomeric methylnitramine $MeNHNO_2$. The difference between the total energies of the isomers is 9.2 kcal mol^{-1} (calculations at the B3LYP 6-311++G(df,pd) level).

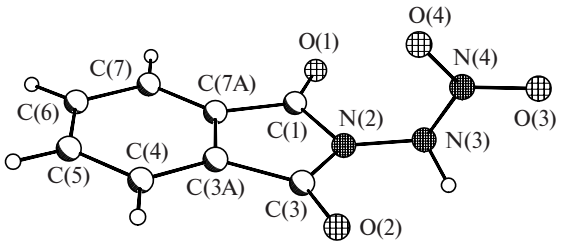


Fig. 1. Molecular structure of *N*-(nitramino)phthalimide **5**.

bonds, which are longer in molecule **5** by 0.01 and 0.02 Å, respectively, due to the presence of the electron-withdrawing substituent at the amine nitrogen atom. At the same time, the N(2)—N(3) bond is substantially shorter than that in *N*-aminophthalimide[18] (1.409 Å) and the calculated bond length in nitrohydrazine[17] (1.390 Å) (Table 2). The N(3)—N(4) bond is substantially elongated compared to those in nitramines (for example, the maximum N—N bond length in cyclotrimethylenetrinitramine is 1.398 Å)[19] and the calculated bond length in nitrohydrazine (1.426 Å). The nitrogen atom N(3) has a pyramidal configuration (the sum of the bond angles is 332.4°). Interestingly, the N(2) atom is also slightly pyramidalized (the sum of the angles is 358.52(9)°) in spite of the fact that its lone electron pair is involved in conjugation with the π system of the phthalimide ring. The N(2)—N(3) bond is noncoplanar with the plane of the phthalimide fragment, and the angle between the plane of the ring and the N(2)—N(3) vector is 9.7°.

The nitramine hydrogen atom H(3N) is involved in a medium-strength intermolecular hydrogen bond with the oxygen atom of the carbonyl group (N(3)...O(1)$_{(0.5-x,0.5+y,0.5-z)}$, 2.864(2) Å; N(3)—H(3N)...O(1), 174° with the N—H distance normalized to 0.87 Å). It should be noted that the intermolecular hydrogen bond is formed with the involvement of the carbonyl oxygen atom rather than the oxygen atom of the nitro group. The molecules are linked to each other by hydrogen bonds to form helical chains running along the crystallographic axis *b* (Fig. 2). In addition to the hydrogen bond, there is the rather strong O(2)...O(4)$_{(x,1+y,z)}$ contact (2.985(2) Å) between the adjacent molecules in the chains.

Since the bond lengths and bond angles in the nitrohydrazine fragment of **5** differ substantially from those observed in nitramines and nitrohydrazine and can be determined by both the structural features of the molecules and the crystal environment, we performed quantum chemical calculations at the B3PW91/6-311G(d,p) level of theory for isolated molecule **5**. A comparison of the molecular geometry determined by X-ray diffraction with the calculated data shows that the observed bond length distribution in the nitrohydrazine fragment in

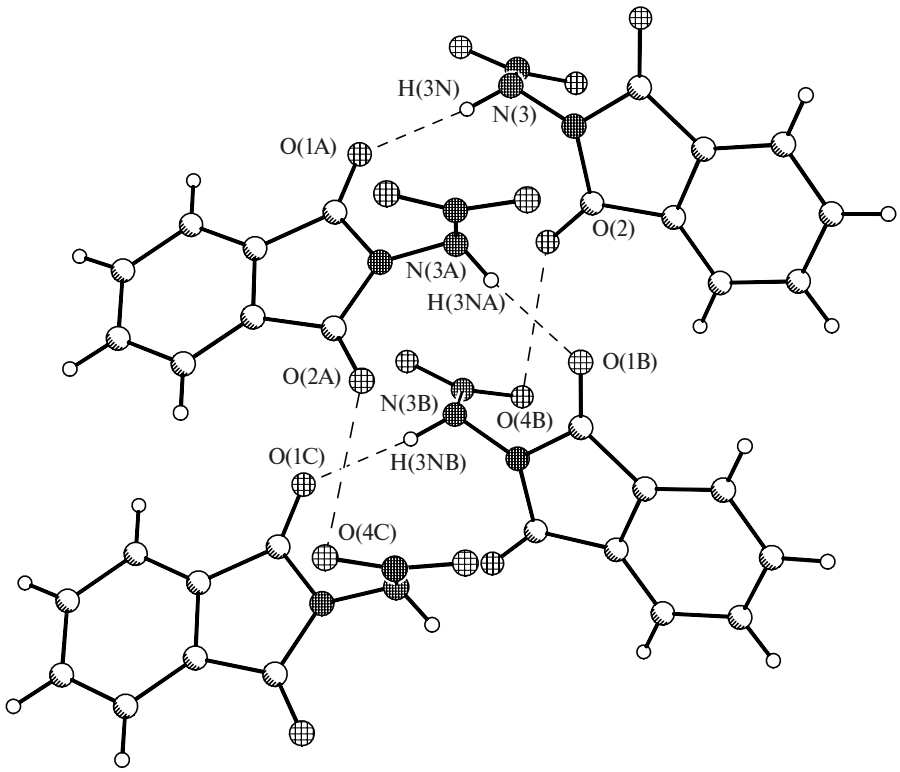


Fig. 2. Fragment of the crystal packing of compound **5** illustrating the intermolecular hydrogen bonding and O(2)...O(4) interactions.

the crystal is virtually identical to that in the gas phase. The maximum difference (0.02 Å) is observed for the N(2)—C(1) bond. In the crystal structure, this bond is shorter than the N(2)—C(3) bond due to the anomeric interaction between the lone electron pair of the N(2) atom and the antibonding orbital of the latter bond (the C(1)—N(2)—N(3)—N(4) torsion angle is 100.56(10)°). In the isolated molecule, the stereoelectronic interaction is virtually absent due to the larger N(2)—N(3) bond length. As in nitramines,[20] the N(3)—N(4) bond length in the condensed state is shorter; however, this decrease is smaller (0.01 Å) than that observed in nitramines (0.06—0.08 Å calculated at the MP2/4-31G level of theory).

Experimental

The ^{1}H, ^{13}C, and ^{14}N NMR spectra were recorded on a Bruker AM-300 instrument operating at 300.13, 75.5, and 21.5 MHz, respectively. The chemical shifts are given relative to $SiMe_4$ (^{1}H and ^{13}C) or $MeNO_2$ (^{14}N, the external standard, upfield chemical shifts are negative). The IR spectra were measured on a Specord M-80 spectrometer. The mass spectra were obtained on a Kratos MS-300 instrument (EI, 70 eV). The progress of the reactions was monitored by TLC (Silufol UV-254 and Merck 60 F_{254}). *N*-Aminophthalimide[21] and an ethereal solution of diazomethane[22] were prepared according to known procedures. The melting points were determined on a Kofler hot-stage apparatus.

X-ray diffraction study of compound 5 was carried out on an automated Bruker APEX II diffractometer (graphite monochromator, λ(Mo-Kα) = 0.71073 Å, θ/2θ-scanning technique, $2\theta_{max}$ = 60°). Colorless crystals ($C_8H_5N_3O_4$, M = 207.15) at T = 100 K are monoclinic, space group $C2/c$, a = 17.3341(11), b = 5.7354(4), c = 18.6716(12) Å, b = 111.337(5)°, V = 1729.1(2) Å^3, Z = 8 (Z' = 1), d_{calc} = 1.320 g cm^{-3}. The structure was solved by direct methods and refined by the full-matrix least-squares methods based on F^2_{hkl} with anisotropic displacement parameters for all nonhydrogen atoms. The hydrogen atoms were located in difference Fourier maps and refined using a riding model. The final R factors were R_1 = 0.0354 (calculated based on F^2 for 2110 observed reflections with $I > 2\sigma(I)$), wR_2 = 0.0988, GOOF = 1.029; the number of refinement parameters was 136. The calculations were carried out with the use of the SHELXTL PLUS program package.

The quantum chemical calculations for molecule **5** were performed with the use of the PC GAMESS program package.[23] The full geometry optimization was carried out at the B3PW91/6-311G(d,p) level of theory; the convergence limit for the average force gradient was $1 \cdot 10^{-5}$ a.u.

2-(Nitramino)-1*H*-isoindole-1,3(2*H*)-dione (5). Nitronium tetrafluoroborate (1.72 g, 13 mmol) was added portionwise with vigorous stirring to a solution of *N*-aminophthalimide (1.50 g, 9.3 mmol) in dry acetonitrile (50 mL) at −30 °C. Then the cooling bath was removed, and the reaction mixture continued to be stirred until the temperature raised to 0 °C. Then the reaction mixture was poured into a mixture of ice water (50 g) and Et_2O (50 mL). A solution of $NaHCO_3$ (4 g) in water (20 mL) was added with stirring. The aqueous layer was separated, washed with Et_2O (2×30 mL), acidified with an aqueous HCl solution (15%) to pH 2, and extracted with CH_2Cl_2 (3×50 mL). The extract was washed with a sodium chloride brine (50 mL), dried ($MgSO_4$), and concentrated *in vacuo*. Nitrohydrazine **5** was obtained in a yield of 1.58 g (82%) as white crystals, m.p. 79—81 °C (decomp.); after recrystallization from benzene, m.p. 82—84 °C (decomp.). Found (%): C, 46.36; H, 2.42; N, 20.25. $C_8H_5N_3O_4$. Calculated (%): C, 46.39; H, 2.43; N, 20.29. IR (KBr), ν/cm^{-1}: 1384, 1628 (both bands of NO_2); 1732 (C=O). ^{1}H NMR ($CDCl_3$), δ: 7.87—7.93 (m, 2 H, Ar); 7.99—8.05 (m, 2 H, Ar); 9.95 (br.s, 1 H, NH). ^{13}C NMR (acetone-d_6), δ: 125.2 (C(4), C(7)); 130.7 (C(3a), C(7a)); 136.7 (C(5), C(6)); 164.6 (C(1), C(3)).

Potassium salt of 2-(nitramino)-1*H*-isoindole-1,3(2*H*)-dione (6). A solution of KOH (54 mg, 0.97 mmol) in MeOH (1 mL) was added dropwise with stirring to a solution of nitrohydrazine **5** (200 mg, 0.97 mmol) in MeOH (1 mL) at 20 °C, after which a white substance precipitated. The mixture was cooled to −20 °C, and the precipitate was filtered off, washed with MeOH (2×1 mL), and dried in air. Potassium salt **6** was obtained in a yield of 182 mg (77%) as a white powder, m.p. 265—285 °C (decomp.). After recrystallization from $MeOH/H_2O$ (1 : 1), colorless needle-like crystals were obtained, m.p. 268—286 °C (decomp.). Found (%): C, 39.06; H, 1.59; N, 17.22; K, 16.36. $C_8H_4N_3O_4K$. Calculated (%): C, 39.18; H, 1.64; N, 17.13; K, 15.94. IR (KBr), ν/cm^{-1}: 1716 (C=O). ^{1}H NMR (D_2O), δ: 7.60—7.70 (m, 4 H, Ar). ^{13}C NMR (D_2O), δ: 123.5 (C(4), C(7)); 129.5 (C(3a), C(7a)); 134.9 (C(5), C(6)); 166.9 (C(1), C(3)).

Table 2. Selected bond lengths (d) and bond angles (ω) in molecule **5** determined by X-ray diffraction and calculated at the B3PW91/6-311G(d,p) level of theory

Parameter	X-ray diffraction	B3PW91/6-311G(d,p)
Bond	*d*/Å	
O(1)—C(1)	1.2114(12)	1.196
O(2)—C(3)	1.2015(14)	1.202
O(3)—N(4)	1.2140(15)	1.205
O(4)—N(4)	1.2098(14)	1.201
N(2)—N(3)	1.3647(12)	1.354
N(2)—C(1)	1.4003(13)	1.421
N(2)—C(3)	1.4229(13)	1.415
N(3)—N(4)	1.4467(12)	1.456
C(3)—C(3A)	1.4764(16)	1.481
C(3A)—C(4)	1.3845(15)	1.384
C(3A)—C(7A)	1.3989(16)	1.394
C(4)—C(5)	1.390(2)	1.395
C(5)—C(6)	1.394(2)	1.396
Angle	ω/deg	
N(2)—C(1)—C(7A)	104.90(9)	103.8
N(2)—C(1)—O(1)	125.10(9)	125.9
N(2)—N(3)—N(4)	111.47(8)	113.8
C(1)—N(2)—C(3)	113.03(9)	113.2
C(1)—N(2)—N(3)	121.87(8)	123.1
N(3)—N(4)—O(3)	113.66(10)	116.8
N(2)—C(3)—C(3A)	104.32(9)	104.7
C(3)—C(3A)—C(4)	129.69(11)	129.6
C(3)—C(3A)—C(7A)	109.01(9)	108.8

Reaction of compound 5 with diazomethane. A solution of diazomethane in Et_2O (3 mL), which was prepared from *N*-methyl-*N*-nitrosourea (0.1 g), was added dropwise to a stirred solution of nitrohydrazine **5** (150 mg, 0.72 mmol) in Et_2O (1 mL) at 0 °C until the gas evolution ceased and the solution turned yellowish. Then the solvent was removed *in vacuo*. A mixture of *N*- and *O*-methyl derivatives **7** and **8** was obtained in a yield of 160 mg (99%) as white crystals. This mixture was separated by preparative TLC (silica gel; $CHCl_3$ as the eluent). *N*-Methyl derivative **7**, m.p. 84—86 °C (after recrystallization from MeOH, m.p. 85—87 °C) was obtained in a yield of 100 mg (63%); a mixture of the *E* and *Z* isomers of *O*-methyl derivative **8** (after recrystallization from MeOH, m.p. 125—140 °C (decomp.)), in a yield of 60 mg (37%).

2-[Methyl(nitro)amino]-1*H*-isoindole-1,3(2*H*)-dione (7). Found (%): C, 48.95; H, 3.17; N, 18.85. $C_9H_7N_3O_4$. Calculated (%): C, 48.87; H, 3.19; N, 19.00. IR (KBr), ν/cm^{-1}: 1384, 1568 (both bands of NO_2); 1740 (C=O). ^1H NMR ($CDCl_3$), δ: 3.85 (s, 3 H, Me); 7.85—7.89 (m, 2 H, Ar); 7.93—7.97 (m, 2 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 43.0 (C(8)); 124.6 (C(4), C(7)); 129.6 (C(3a), C(7a)); 135.5 (C(5), C(6)); 163.6 (C(1), C(3)). ^{14}N NMR ($CDCl_3$), δ: −28 ($\Delta\nu_{1/2}$ = 30 Hz, NO_2). MS, *m/z*: 175 $[M - NO_2]^+$.

2-[Methoxy(oxido)diazenyl]-1*H*-isoindole-1,3(2*H*)-dione (8). Mixture of *E*/*Z* isomers, 4 : 1. Found (%): C, 49.01; H, 3.20; N, 19.11. $C_9H_7N_3O_4$. Calculated (%): C, 48.87; H, 3.19; N, 19.00. MS, *m/z*: 221 $[M]^+$.

Isomer *E*-**8**. ^1H NMR ($CDCl_3$), δ: 4.19 (s, 3 H, Me); 7.78—7.84 (m, 2 H, Ar); 7.89—7.94 (m, 2 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 58.9 (CH_3); 124.0 (C(4), C(7)); 130.5 (C(3a), C(7a)); 134.7; 134.8 (C(5), C(6)); 161.9 (C(1), C(3)). ^{14}N NMR ($CDCl_3$), δ: −40 ($\Delta\nu_{1/2}$ = 200 Hz, N→O).

Isomer *Z*-**8**. ^1H NMR ($CDCl_3$), δ: 4.05 (s, 3 H, Me); 7.78—7.84 (m, 2 H, Ar); 7.89—7.95 (m, 2 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 58.3 (CH_3); 124.0 (C(4), C(7)); 130.5 (C(3a), C(7a)); 134.7, 134.8 (C(5), C(6)); 161.9 (C(1), C(3)).

Thermal decomposition of 2-(nitramino)-1*H*-isoindole-1,3(2*H*)-dione (5) *in vacuo*. Synthesis of 2*H*-3,1-benzoxazine-2,4-(1*H*)-dione (isatoic anhydride) (9). Nitrohydrazine **5** (120 mg, 0.58 mmol) was dissolved in CH_2Cl_2 (50 mL). The solution was placed in a 500-mL flask. The solvent was evaporated *in vacuo* in such a way that the compound was uniformly distributed over the walls of the flask in a layer as thin as possible. Then the vacuum was created in the flask with the use of a water-jet aspirator pump, and the flask was placed in an oil bath preheated to 80 °C. The oil bath was heated at 80 °C → 100 °C for 5 min. After completion of heating, the flask was cooled, and the solid residue (94 mg) was separated by preparative TLC (silica gel; $CHCl_3$/EtOAc, 4 : 1, as the eluent). Compound **9** was obtained as a white powder in a yield of 40 mg (42%), m.p. 220—230 °C (decomp.); after recrystallization from ethanol, m.p. 238—242 °C (decomp.) (lit. data[15]: m.p. 240—243 °C (decomp.)). The IR and mass spectra are identical to the data obtained earlier.[16] ^1H NMR (DMSO-d_6), δ: 7.12 (d, 1 H, *J* = 8.1 Hz); 7.22 (t, 1 H, *J* = 7.3 Hz); 7.70 (dt, 1 H, *J* = 7.3 Hz, *J* = 1.5 Hz); 7.86 (d, 1 H, *J* = 8.1 Hz); 11.7 (br.s, 1 H, NH) (*cf.* Ref. 16). ^{13}C NMR (DMSO-d_6), δ: 110.0; 115.2 (CH); 123.6 (CH); 128.8 (CH); 136.9 (CH); 141.1; 147.0; 159.8.

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