

2,6-Dithiodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine and Related Dioxo- and Diimino-decahydrodiimidazopyrazines

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ABSTRACT

Thiourea condensed with 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine **2** in the presence of hydrochloric acid to give 2,6-dithiodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine **5** isolated as the dihydrochloride salt. The salt **5**·2*HCl* was converted to the free base **5** by lithium hydroxide, to the dinitrate salt **5**·2*HNO*₃ by silver nitrate, degraded to 2-thio-2,3,4,7-tetrahydro-1*H*-imidazo[4,5-*b*]pyrazine **6** in a reaction with tert-butyl amine, and converted to 4,8-dihydro-4,8-dinitro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine-2,6-disulfonic acid **9** by nitric acid (100%) at -40°C. Denitration of the dinitramine **9** to give 4,8-dihydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine **11** was brought about by methanolic hydrogen chloride in ether. In one run nitration without oxidation converted the salt **5**·2*HCl* to the dinitrate salt of the 4,8-dinitro derivative **10**; treatment with triethyl amine liberated the free base **10** from the salt. Degradation of 2,6-dioxo-1,3,4,5,7,8-hexanitrodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine **12** to 2-oxo-2,3-dihydro-1,3-dinitro-1*H*-imidazo[4,5-*b*]pyrazine **13** was brought about by hydrochloric acid. Treatment with lithium hydroxide also liberated 2,6-dioxodecahydro-1*H*,5*H*-diimidazo [4,5-*b*:4',5'-*e*]pyrazine **3** from its dihydrochloride salt. Attempts to liberate 2,6-diiminodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine **4** from its tetrahydrochloride salt led instead to intractable mixtures. The tetrahydrochloride salt **4**·4*HCl* was converted to the dihydrochloride salt **4**·2*HCl* in a reaction with tert-butyl amine.

INTRODUCTION

The discovery of dioxo and diimino derivatives **3** and **4** of decahydrodiimidazopyrazine, isolated as hydrochloride salts, introduced the new ring system 1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine **1** [1,2]. These unique derivatives of piperazine were obtained from 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine **2** [3] in condensations with urea and guanidine. Nitration of the heterocycles **3** and **4** gave examples of polynitramines [1,2], a class of compounds with an ongoing appraisal of its contribution to superior energetic materials [4]. The preparation of 2,6-dithiodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine **5** and a comparison of certain properties of the related heterocycles **3**, **4**, and **5** were undertaken in the present investigation.

RESULTS AND DISCUSSION

Tetrahydroxypiperazine **2** combined with thiourea in the presence of hydrochloric acid to give an amorphous colorless solid. Analogy with the similar formations of salts **3**·2*HCl* and **4**·4*HCl* from urea and guanidine and elemental analysis permitted identification of the product as a dihydrochloride salt **5**·2*HCl* of 2,6-dithiodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine **5**, an assignment supported by chemical transformations and spectroscopic analyses. An efficient conversion of the salts **3**·2*HCl* and **5**·2*HCl* to the heterocycles **3** and **5** was brought about by mild treatment with lithium hydroxide [5] in sharp contrast with the intractable mixtures obtained in attempted neutralizations with other alkaline reagents. A similar

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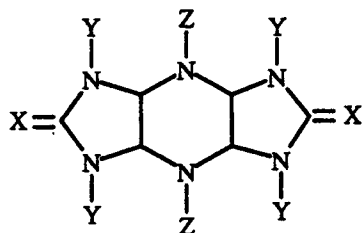
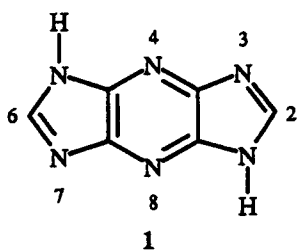
treatment of the salt $4 \cdot 4\text{HCl}$ with lithium or sodium hydroxide also gave unidentifiable material, reminiscent of the difficulties often encountered in the isolation of a guanidine base; however, partial neutralization of the guanidine salt $4 \cdot 4\text{HCl}$ gave the new salt $4 \cdot 2\text{HCl}$ by treatment with *tert*-butylamine. Regeneration of the salt $5 \cdot 2\text{HCl}$ was brought about by the combination of the heterocycle **5** and hydrogen chloride in methanol.

Assignment of the bithiourea structure **5** was supported by the ^{13}C NMR signals for the thiocarbonyl carbon atom at δ 181.66 and 180.91 [6]; a similar signal at δ 183.81 was obtained for thiourea. For the bithiourea dihydrochloride $5 \cdot 2\text{HCl}$, a shift in the ^{13}C NMR signal to δ 167.81 resembled a corresponding shift to δ 174.03 for thiourea hydrochloride. Infrared absorption in the two regions 1430–1650 and 1100–1225 cm^{-1} characteristic of a thioamide moiety [7] was also supportive of the structures **5** and $5 \cdot 2\text{HCl}$. For thiourea hydrochloride its absorption at 1654 cm^{-1} without concurrent absorption in the 1100–1225 cm^{-1} region was observed.

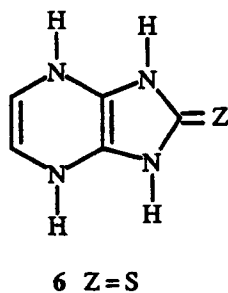
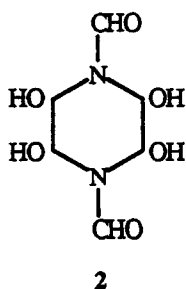
Attempts to identify products in the complex mixtures obtained from combining primary amines, with and without the presence of mercuric oxide [8] or lead oxide [9], with the salt $5 \cdot 2\text{HCl}$ were generally unsuccessful. Treatment with *tert*-butylamine degraded the salt to a compound, $\text{C}_5\text{H}_6\text{N}_4\text{S}$ mw 154, assigned the structure of 2-thio-2,3,4,7-tetrahydro-1*H*-imidazo[4,5-*b*]pyrazine **6** otherwise detected in the EI-MS analyses of **5** and $5 \cdot 2\text{HCl}$ in which m/z signals at 154, 95, 76, 60, and 43 were

respectively assigned to the heterocycle **6** (or tautomer), aminopyrazine **7** ($\text{C}_4\text{H}_5\text{N}_3$), thiourea ($\text{CH}_2\text{N}_2\text{S}$), protonated hydrogen isothiocyanate (CH_2NS), and protonated carbodiimide (CH_3N_2). A similar fragmentation pattern for the salt $4 \cdot 4\text{HCl}$ showed m/z signals at 137 and 59 assigned to 2-imino-2,3,4,7-tetrahydro-1*H*-imidazo[4,5-*b*]pyrazine **8** (or tautomer) and guanidine (CH_5N_3).

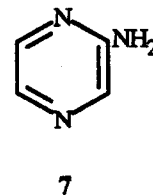
Treatment with silver nitrate converted the salt $5 \cdot 2\text{HCl}$ to the salt $5 \cdot 2\text{HNO}_3$. The latter was presumably an intermediate [10] in a conversion of the salt $5 \cdot 2\text{HCl}$ by treatment with nitric acid (100%) at -40°C to a product assigned the structure of zwitterionic 4,8-dihydro-4,8-dinitro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine-2,6-disulfonic acid **9** or to 2,6-dithiododecahydro-4,8-dinitro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine **10**. The complex overall conversion to the zwitterion **9** required dehydrogenation, oxidation, and *N*-nitration. In marked contrast similar treatment cleanly converted the bisurea **3** and the bisguanidine **4** to poly-*N*-nitro derivatives in good yields without detectable competition from dehydrogenation and oxidation [1,2]. The reaction between the bithiourea **5** and nitric acid was in agreement with resistance of thiourea moieties to undergo *N*-nitration [10,11] and with oxidations of thiones to sulfonic acids [12–21]. Although the conversion of the salt $5 \cdot 2\text{HCl}$ to the sulfonic acid **9** was reproducible one maverick run led to the formation of the dinitramine **10** as the dinitrate salt without a trace of the formation of the acid **9**. Treatment with triethyl amine liberated the free base **10** from the salt $10 \cdot 2\text{HNO}_3$.

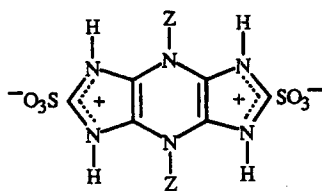


- 3 X=O, Y=Z=H
 4 X=NH, Y=Z=H
 5 X=S, Y=Z=H
 10 X=S, Y=H, Z=NO₂
 12 X=O, Y=Z=NO₂

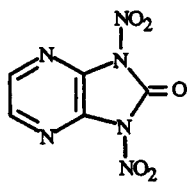


- 6 Z=S
 8 Z=NH



9 Z = NO₂

11 Z = H



13

Denitration of the dinitramine **9** to 4,8-dihydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine-2,6-disulfonic acid **11** was brought about in a reaction with methanolic hydrogen chloride. Both of the stable dihydrodiimidazopyrazines **9** and **11** are derivatives of the electron rich "antiaromatic" 1,4-dihydropyrazine [22–24], and the dinitro compound **9** is also related to the rarely encountered α,β -unsaturated nitramines [25]; the elusive enedinitramine moieties offer superior calculated properties for energetic material [1]. Although hydrolytic conversion of a nitramine to an amine has been infrequently observed [1,26], a similar mild treatment with hydrochloric acid degraded the hexanitrobisurea **12** to a compound tentatively assigned the structure of 2-oxo-2,3-dihydro-1,3-dinitro-1*H*-imidazo[4,5-*b*]pyrazine **13** isolated as a tetrahydrate.

EXPERIMENTAL

Instruments included: Pye-Unicam SP 200 IR, Perkin Elmer 1600 series FTIR, JEOL FX 90Q NMR, Varian Gemini-300 NMR, Hewlett-Packard 5985 (70 eV) (GC-MS), and Vestec Electrospray 201 (LC-MS). ¹H NMR spectra were run in deuterated solvents with tetramethylsilane as an internal standard. ¹³C NMR were recorded at 22.5 MHz with the deuterated solvent as an internal reference; the central peak of the solvent multiplet signal was assigned: δ 77.00 (CDCl₃), δ 39.50 (CD₃)₂(SO), and δ 29.8 (CD₃)₂(CO). Melting points were determined on a Mel-Temp II melting point apparatus and were uncorrected. Elemental analyses were obtained from Midwest Micro Lab, Indianapolis, IN, and Galbraith Laboratories, Knoxville, TN. Solvents were removed by rotary evaporation under reduced pressure unless indicated otherwise. Column chromatography was performed on silica gel (various grades). The reported EI-MS and electrospray ionization (ESI-MS) data were restricted to major *m/z* values and to M⁺ when detected. 1,4-Diformyl-2,3,5,6-tetrahydropiperazine **2** was obtained from a condensation between formamide and glyoxal [3].

N-Nitro compounds should be handled as potentially explosive materials.

2,6-Dithiodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine **5**

1,4-Diformyl-2,3,5,6-tetrahydropiperazine **2** (4.10 g, 0.020 mol) was added in portions over a period of 10 minutes with stirring to a solution of thiourea (9.0 g, 0.12 mol) in concentrated hydrochloric acid (30 mL). The reaction mixture was stirred at 25°C for 2 days. A solid was isolated, washed with absolute alcohol (3 × 20 mL), dried, and purified by dissolving in methanol followed by concentration to give 2,6-dithiodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine **5** as an amorphous dihydrochloride (2.85 g, 47%), mp 175–177°C (dec). IR (KBr) ν /cm⁻¹: 3292–3107, 1630 (C=S) [7], 1430, 1412, 1367, 1306, 1109 (C=S) [7], 1049, 947, 884, 738. ¹H NMR (DMSO-*d*₆): δ 9.23 (bs, 4H, exchangeable with D₂O), 5.12 (s, 4H, CH), and 4.62 (s, 4H, exchangeable with D₂O). ¹³C NMR (DMSO-*d*₆): δ 167.81 (C=S), 62.65, 61.42. EI-MS, *m/z* (relative intensity): 154 (100), 95 (55), 76 (93), 60 (41), 43 (37), and 36 (49). Anal. calcd for C₆H₁₂N₆Cl₂S₂ mw 303: C, 23.77; H, 3.99; N, 27.72; Cl, 23.38; S, 21.15. Found: C, 23.43; H, 3.92; N, 27.07; Cl, 22.98; S, 21.03. Comparable values were obtained for thiourea hydrochloride mp 136°C [27]. IR (KBr) ν /cm⁻¹: 3308, 1654 (C=S), 1438, 1396. ¹³C NMR (DMSO-*d*₆/H₂O): δ 174.03.

Silver nitrate (0.73 g, 4.3 mmol) in distilled water (3 mL) was added to a solution of the salt **5**·2HCl (0.65 g, 2.1 mmol) in distilled water (15 mL). The reaction mixture was stirred for 10 minutes. A precipitate of silver chloride was isolated and washed with distilled water (3 mL). The combined mother liquor and filtrate was evaporated to one-tenth volume and treated with absolute alcohol. A precipitate was isolated and washed with distilled water (1 mL) and absolute alcohol (10 mL) and dried to give the dinitrate salt **5**·2HNO₃ (0.39 g, 51%), mp 165–170°C (dec). IR (KBr) ν /cm⁻¹: 3314–3143, 1637 (C=S) [7], 1596, 1384, 1326, 1184, 1126 (C=S) [7], 1048, 950, 826, 748, 665. ¹H NMR (DMSO-*d*₆): δ 8.76 (bs, 4H, exchangeable with D₂O), 4.90 (s, 4H, CH), 4.40 (bs, 4H, exchangeable with D₂O). ¹³C NMR (DMSO-*d*₆): δ 167.61 (C=S), 62.46, 61.48. Anal. calcd for C₆H₁₂N₆O₆S₂: C, 20.23; H, 3.37; N, 31.46; S, 17.98. Found: C, 20.44; H, 3.42; N, 31.20; S, 18.21.

tert-Butylamine (5 mL) was added at 25°C to a stirred suspension of the salt **5**·2HCl (1.00 g, 3.3 mmol) in methanol (75 mL). Stirring of the clear reaction mixture was continued for 2 days at the same temperature as 2-thio-2,3,4,7-tetrahydro-1*H*-imidazo[4,5-*b*]pyrazine **6** precipitated as a colorless solid (0.28 g, 55%), mp 235–240°C (dec) after it was washed with water (5 mL) and methanol (2

× 10 mL) and dried. IR (KBr) ν/cm^{-1} : 3280–3060, 1600 (C=S) [7], 1520, 1450, 1335, 1140 (C=S) [7], 1085, 1055, 1020, 835. ^1H NMR (DMSO- d_6): δ 8.57 (s), 8.20 (s), and 3.37 (s, exchangeable with D_2O) (estimated ratio of tautomers 1.5:0.5). ^{13}C NMR (DMSO- d_6): 180.75 (C=S) [6], 149.40, 139.78, 137.44, 136.01. EI-MS, m/z (relative intensity): 154 (100), 137 (7), 121 (7), 95 (41), 79 (8), 68 (38), 60 (14). Anal. calcd for $\text{C}_5\text{H}_6\text{N}_4\text{S}$: C, 38.96; H, 3.90; N, 36.36; S, 20.78. Found: C, 39.23; H, 3.83; N, 34.93 (assumed to be in error); S, 20.40.

Lithium hydroxide (1.0 N, 20 mL) was added to a suspension of 2,6-dithiododecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine dihydrochloride **5**·2HCl (3.0 g, 10 mmol) in tetrahydrofuran (100 mL) with stirring at 0°C. After stirring was continued for 30 minutes at 10–15°C, a precipitate was isolated, washed with distilled water (3 × 15 mL) and ethanol (10 mL), and dried to give 2,6-dithiododecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine **5** (1.3 g, 54%) (dimethyl sulfoxide/chloroform) as an amorphous colorless solid, mp 175–185°C (dec). IR (KBr) ν/cm^{-1} : 3307, 3186, 1631 (C=S) [7], 1595, 1523, 1337, 1192 (C=S) [7], 975. ^1H NMR (DMSO- d_6): δ 8.43 (s, exchangeable with D_2O), 8.30 (s, exchangeable with D_2O), 4.78 (s, exchangeable with D_2O), 4.64 (s), 4.14 (s), 2.30 (s, exchangeable with D_2O) (estimated ratio of tautomers 3:2). ^{13}C NMR (DMSO- d_6): δ 181.66 (C=S) [6], 180.91 (C=S) [6], 68.97, 64.69. EI-MS, m/z (relative intensity): 154 (22) (**6**, see above), 95 (62), 76 (85), 68 (62), 59 (100), 43 (63). Anal. calcd for $\text{C}_6\text{H}_{10}\text{N}_6\text{S}_2$: C, 31.30; H, 4.35. Found: C, 30.74; H, 4.46. Comparable values were obtained for thiourea. IR (KBr) ν/cm^{-1} : 3386–3176, 1618 (C=S), 1473, 1084 (C=S), 780. ^{13}C NMR (DMSO- $d_6/\text{H}_2\text{O}$): δ 183.81.

Ethereal hydrogen chloride (saturated, 5 mL) was added to the bithiourea derivative **5** (0.10 g, 0.40 mmol) in dry methanol (25 mL) at 0°C with stirring. The stirring was continued for 10 minutes at 25°C. The solvent was removed to give **5**·2HCl (0.12 g, 92%), mp 175–177°C (dec).

Lithium hydroxide (1.0 N, 10 mL) was added to a suspension of 2,6-dioxodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine dihydrochloride **3**·2HCl [**2**] (1.3 g, 5.0 mmol) in tetrahydrofuran (100 mL) with stirring at 0°C as the solution became clear. Stirring was continued for 30 minutes at 10–15°C. A precipitate was isolated, washed with distilled water (3 × 15 mL) and ethyl alcohol (10 mL), and dried to give 2,6-dioxodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine **3** (0.56 g, 57%), mp 221–223°C (dec). IR (KBr) ν/cm^{-1} : 3468, 3315, 3217, 1685 (C=O), 1474, 1265, 1163. ^1H NMR (DMSO- d_6): δ 6.21 (s, 4H, NH, exchangeable with D_2O), 4.38–4.40 (m, 6H, 4CH and 2NH, partially exchangeable with D_2O). EI-MS, m/z (relative intensity): 95 (32), 81 (38), 69 (100), 60 (91), 44 (91). Anal. calcd for $\text{C}_6\text{H}_{10}\text{N}_6\text{O}_2$: C, 36.36; H, 5.05; N, 42.42. Found: C, 36.12; H, 5.01; N, 42.25.

2,6-Diiminodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine dihydrochloride **4**·2HCl

To a well-stirred suspension of 2,6-diiminodecahydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine tetrahydrochloride **4**·4HCl [**1**] (1.30 g, 3.8 mmol) in methanol (75 mL), *tert*-Butylamine (1.70 g, 23 mmol) at 0–5°C was added and stirring was continued for 24 hours at 25°C. A solid was isolated, washed with methanol (10 mL), and dried to give the dihydrochloride **4**·2HCl (0.65 g, 63%), mp 210–220°C (charred) (methanol/water). IR (KBr) ν/cm^{-1} : 3284, 3237, 3179, 3117, 1684 (C=N), 1582, 1142, 1109. ^1H NMR (DMSO- d_6): δ 7.97 (bs, 4H, exchangeable with D_2O), 7.58 (bs, 4H, exchangeable with D_2O), 4.96 (s, 4H, CH), and 4.15 (bs, 2H, exchangeable with D_2O). Anal. calcd for $\text{C}_6\text{H}_{14}\text{N}_8\text{Cl}_2$: C, 26.77; H, 5.21; N, 41.65; Cl, 26.37. Found: C, 26.83; H, 5.29; N, 41.39; Cl, 25.71. An X-ray crystallographic confirmation for the structure **4**·2HCl will be published elsewhere.

4,8-Dihydro-4,8-dinitro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine-2,6-disulfonic Acid **9**

The salt **5**·2HCl (3.0 g, 0.01 mol) was added in portions over a period of 10 minutes at –40°C to stirred nitric acid (100%, 50 mL), and stirring was continued for 1 hour at –40°C and 2 hours at 25°C. The reaction mixture was poured onto crushed ice and left standing for 17 hours as the zwitterionic acid **9** precipitated and was washed with ice-water and dried to give an amorphous colorless solid (0.72 g, 18%), mp 156–160°C (dec) after purification from acetone/chloroform. IR (KBr) ν/cm^{-1} : 3012, 2024, 1701, 1595, 1270, 1118, 1082, 990, 910, 791, 629. ^1H NMR (CDCl_3): δ 7.40 (s) and 6.59 (s) (intensity 1:1, exchangeable with D_2O). ^{13}C NMR (acetone- d_6): δ 146.35, 146.26, 83.06, 82.00, 67.87, 66.32. EI-MS, m/z (relative intensity): 354 (15), 308 (10), 250 (11), 150 (17), 148 (26), 142 (23), 114 (15), 112 (21), 104 (18), 84 (18), 79 (9), 59 (22), 46 (100). Anal. calcd for $\text{C}_6\text{H}_8\text{N}_8\text{O}_{10}\text{S}_2$: C, 17.48; H, 0.97; N, 27.18; O, 38.83; S, 15.53. Found: C, 17.71; H, 1.01; N, 26.78; O, 38.50; S, 15.84.

The preparation of the product **9** was reproducible, however in one maverick run, addition of the salt **5**·2HCl (2.00 g, 6.6 mmol) with stirring to nitric acid (100%, 30 mL) at –40°C was followed by stirring at the same temperature for 2 hours to give a mixture that was poured onto crushed ice and stored for 17 hours at 25°C as the dinitrate salt of 2,6-dithiododecahydro-4,8-dinitro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine **10** precipitated. It was washed with ice-water and dried to give an amorphous colorless solid (0.95 g, 32%), mp 228–233°C (dec) (dimethyl sulfoxide/chloroform). IR (KBr) ν/cm^{-1} : 3008, 1606 (C=S) [7], 1384, 1309, 1271, 1165 (C=S) [7], 1084, 1018, 993, 939, 753, 709. ^1H NMR (DMSO- d_6): δ 8.90 (bs, 2H, exchangeable with D_2O),

7.04 (bs, 4H, exchangeable with D₂O), 6.47 (s, 4H, CH). ¹³C NMR (DMSO-*d*₆): δ 160.39, 67.27, 58.68. EI-MS, *m/z* (relative intensity): 274 (13), 228 (3), 114 (97), 60 (100), 45(27). Anal. calcd for C₆H₁₀N₁₀O₁₀S₂: C, 16.14; H, 2.24; N, 31.39. Found: C, 16.61; H, 2.40; N, 31.05.

Triethylamine (0.23 g, 2.3 mmol) was added at 0°C to a suspension of the dinitrate **10**·2HNO₃ (0.50 g, 1.1 mmol) in absolute methanol (75 mL). After stirring for 17 hours at 25°C, a precipitate was filtered, washed with absolute methanol (5 mL), and dried to give the free base **10** (0.32 g, 89%), mp 265–274°C (dec) (dimethyl sulfoxide/chloroform). IR (KBr) ν/cm^{-1} : 3441, 3289, 2988, 1648 (C=S) [7], 1597, 1559, 1310, 1288, 1194 (C=S) [7], 1117, 1069, 985, 930, 771, 718. ¹H NMR (DMSO-*d*₆): δ 6.70 (s, exchangeable with D₂O), 6.64 (s, exchangeable with D₂O), 6.58 (s, exchangeable with D₂O), 6.23 (s), 6.17 (s), 6.09 (s) (estimated ratio of tautomers 5:3.5:2). ¹³C NMR (DMSO-*d*₆): δ 150.77, 71.50, 57.84. Anal. calcd for C₆H₈N₈O₄S₂: C, 22.50; H, 2.50; N, 35.00; S, 20.00. Found: C, 22.41; H, 2.51; N, 35.29; S, 20.25.

Saturated ethereal hydrogen chloride (5 mL) was added slowly at 0–5°C to a stirred solution of the dinitramine **9** (0.60 g, 1.5 mmol) in absolute methanol (75 mL). Stirring for 17 hours at 25°C brought about the formation of a precipitate. After isolation it was washed with absolute methanol (2 × 5 mL) and dried to give 4,8-dihydro-1*H*,5*H*-diimidazo[4,5-*b*:4',5'-*e*]pyrazine-2,6-disulfonic acid **11** as a colorless solid (0.17 g, 37%), mp 190–195°C (dec). IR (KBr) ν/cm^{-1} : 3235, 3104, 2972, 2850, 1685, 1645, 1609, 1271, 986, 925, 774, 714, 628. ESI-MS [MeOH-H₂O]: 367 (M – H + 2Na)⁺, 345 (M + Na)⁺. Anal. calcd for C₆H₆N₆O₆S₂: C, 22.36; H, 1.86; N, 26.08; O, 29.81; S, 19.88. Found: C, 22.61; H, 2.05; N, 24.15; O, 30.07; S, 18.67 (analyses for N and S assumed to be in error). Insufficient solubility in common solvents and decomposition in dimethyl sulfoxide, *N,N*-dimethylformamide, and trifluoroacetic acid precluded NMR spectroscopy.

2-Oxo-2,3-dihydro-1,3-dinitro-1*H*-imidazo[4,5-*b*]pyrazine **13**

The hexanitrobisurea **12** (2.0 g, 4.3 mmol) was added in portions to a stirred solution of concentrated hydrochloric acid (37%, 15 mL) at 25°C and the stirring was continued for 2 hours at the same temperature. The solvent was removed under reduced pressure to give a highly hygroscopic compound tentatively assigned the structure of the dinitrourea **13** (0.21 g, 17%), mp 176–180°C (dec). IR (KBr) ν/cm^{-1} : 3400, 1780, 1560, 1260, 1100, 830. ¹H NMR (acetone-*d*₆): δ 6.18–7.17 (m). Anal. calcd for C₅H₁₀N₆O₉: C, 20.13; H, 3.36; N, 28.19. Found: C, 20.28; H, 3.18; N, 27.70.

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FOOTNOTES AND REFERENCES

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