Experimental Section

Melting points are uncorrected. Yields are isolated yields. A Halos high pressure mercury lamp (1000 W) was used as an irradiation source.

General Procedure for Synthesis of *N,N'*-Dialkylpiperazinetetrones 1. *N,N'*-Dialkyloxamide (1 g) and oxalyl chloride (5 g) was placed in a sealed tube and heated to 120 °C for 4 h. The excess oxalyl chloride was removed by evaporation under reduced pressure, and the residue was recrystallized from acetonitrile–benzene.

1,4-Dimethylpiperazinetetrone (1a) has been reported.[14]

1,4-Diethylpiperazinetetrone (1b): mp 210–211 °C; IR (KBr) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12 (t, 6 H, J = 7 Hz, CH_3), 3.77 (q, 4 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 11.7 (q), 35.8 (t), 153.9 (s); mass spectrum (CI), m/z 199 (M + 1). Anal. Calcd for $C_8H_{10}N_2O_4$: C, 48.48; H, 5.08; N, 14.13. Found: C, 48.60; H, 5.15; N, 14.20.

1,4-Dipropylpiperazinetetrone (1c): mp 203–207 °C; IR (KBr) 1680 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 0.89 (t, 6 H, J = 8 Hz, CH_3), 1.4–1.8 (m, 4 H, CH_2), 3.68 (t, 4 H, J = 7 Hz, NCH_2); ^{13}C NMR (Me_2SO-d_6) δ 11.4 (q), 20.1 (t), 42.5 (t), 154.4 (s); mass spectrum (CI), m/z 227 (M + 1). Anal. Calcd for $C_{10}H_{14}N_2O_4$: C, 53.09; H, 6.23; N, 12.38. Found: C, 53.09; H, 6.34; N, 12.39.

1,4-Diisobutylpiperazinetetrone (1d): mp 174–175 °C; IR (KBr) 1680 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 0.89 (d, 12 H, J = 7 Hz, CH_3), 1.7–2.2 (m, 2 H, CH), 3.56 (d, 4 H, J = 7 Hz, CH_2); ^{13}C NMR (Me_2SO-d_6) δ 20.3 (q), 26.7 (d), 48.0 (t), 154.6 (s); mass spectrum (CI), m/z 255 (M + 1); UV λ_{max} (CH_3CN) 242 nm (ϵ 14 000) and 330 nm (sh, 80), λ_{max} (C_6H_6) 345 nm (sh, 50). Anal. Calcd for $C_{12}H_{18}N_2O_4$: C, 56.68; H, 7.13; N, 11.01. Found: C, 56.36; H, 7.10; N, 10.91.

General Procedure for Photolysis. A solution of 1 (400 mg) in acetonitrile (40 mL) was deaerated by bubbling through argon and irradiated with a high pressure mercury lamp through a Pyrex filter for 2–4 h. After evaporation of the solvent, products were isolated by chromatography on silica gel.

4-Ethyl-1,4-diaza-7-oxabicyclo[4.3.0]nonane-2,3,5-trione (2b): mp 204–205 °C; IR ($CHCl_3$) 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (t, 3 H, J = 7 Hz, CH_3), 3.5–4.5 (m, 6 H, methylenes), 5.43 (s, 1 H, CH); ^{13}C NMR ($CDCl_3$) δ 12.8 (q), 36.6 (t), 43.7 (t), 65.3 (t), 83.2 (d), 150.6 (s), 156.9 (s), 163.9 (s); mass spectrum (CI), m/z 199 (M + 1). Anal. Calcd for $C_8H_{10}N_2O_4$: C, 48.48; H, 5.08; N, 14.13. Found: C, 48.59; H, 5.11; N, 14.16.

8-Methyl-4-propyl-1,4-diaza-7-oxabicyclo[4.3.0]nonane-2,3,5-trione (2c): mp 105–109 °C; IR ($CHCl_3$) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (t, 3 H, J = 7 Hz, CH_3), 1.49 (d, 3 H, J = 7 Hz, CH_3), 1.3–1.8 (m, 2 H, CH_2), 3.3–4.1 (m, 4 H, NCH_2), 4.3–4.6 (m, 1 H, $OCHCH_3$), 5.52 (s, 1 H, OCHN); ^{13}C NMR ($CDCl_3$) δ 11.2 (q), 18.6 (q), 20.8 (t), 42.9 (t), 50.3 (t), 74.1 (d), 83.4 (d), 150.6 (s), 157.2 (s), 164.0 (s). Anal. Calcd for $C_{10}H_{14}N_2O_4$: C, 53.09; H, 6.23; N, 12.38. Found: C, 52.95; H, 6.26; N, 12.36.

2-Hydroxy-1-(2-propenyl)-4-propylpiperazine-3,5,6-trione (3c): mp 101–102 °C; IR ($CHCl_3$) 3350 and 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (t, 3 H, J = 7 Hz, CH_3), 1.4–1.8 (m, 2 H, CH_2), 3.4–4.1 and 4.3–4.7 (m, 4 H, NCH_2), 5.1–5.5 (m, 3 H, NCHO and olefinic), 5.5–6.0 (m, 1 H, olefinic), 6.1 (br d, 1 H, OH); ^{13}C NMR ($CDCl_3$) δ 11.2 (q), 20.6 (t), 42.7 (t), 46.4 (t), 77.3 (d), 120.5 (t), 130.2 (d), 153.1 (s), 156.3 (s), 166.7 (s); mass spectrum (CI), m/z 227 (M + 1). Anal. Calcd for $C_{10}H_{14}N_2O_4$: C, 53.09; H, 6.23; N, 12.38. Found: C, 52.70; H, 6.21; N, 12.26.

8,8-Dimethyl-4-isobutyl-1,4-diaza-7-oxabicyclo[4.3.0]nonane-2,3,5-trione (2d): mp 141–142 °C; IR ($CHCl_3$) 1685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (d, 6 H, J = 6 Hz, $CHMe_2$), 1.45 (s, 3 H, CH_3), 1.51 (s, 3 H, CH_3), 1.8–2.2 (m, 1 H, CH), 3.1–4.0 (m, 4 H, NCH_2), 5.67 (s, 1 H, NCHO); ^{13}C NMR ($CDCl_3$) δ 20.0 (q), 25.3 (q), 26.8 (q), 26.9 (d), 48.0 (t), 54.9 (t), 81.1 (s), 82.1 (d), 150.5 (s), 157.5 (s), 165.3 (s); mass spectrum (CI), m/z 255 (M + 1). Anal. Calcd for $C_{12}H_{18}N_2O_4$: C, 56.68; H, 7.13; N, 11.01. Found: C, 56.61; H, 7.12; N, 10.96.

2-Hydroxy-1-(2-methyl-2-propenyl)-4-isobutylpiperazine-3,5,6-trione (3d): mp 136–139 °C; IR ($CHCl_3$) 3320 and 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (d, 6 H, J = 6 Hz, $CHMe_2$), 1.71 (s, 3 H, CH_3), 1.9–2.2 (m, 1 H, CH), 3.4–3.9 (m, 2 H, NCH_2), 3.84 and 4.54 (AB q, 2 H, J = 15 Hz, NCH_2), 4.95 (br d, 2 H, olefinic), 5.34 (br d, s on addition of D_2O, 1 H, NCHO), 6.2 (br d, 1 H, OH exchangeable); ^{13}C NMR ($CDCl_3$) δ 20.0 (q), 20.1 (q), 26.8 (d), 47.3 (t), 48.9 (t), 77.1 (d), 114.7 (t), 137.9 (s), 153.5 (s), 156.5 (s), 166.9 (s); mass spectrum (CI), m/z 255 (M + 1). Anal. Calcd for $C_{12}H_{18}N_2O_4$: C, 56.68; H, 7.13; N, 11.01. Found: C, 56.37; H, 7.14; N, 10.93.

Conversion of 3d into 1d. Compound **3d** (100 mg) in ethanol (50 mL) was hydrogenated over Pd–C (5%, 50 mg) for 2 h. The reaction mixture was filtered and evaporated. The crude product was dissolved in pyridine (20 mL) containing CrO_3 (100 mg). The mixture was set aside for 2 h and then treated as usual. The product (62 mg) isolated by chromatography was proved to be **1d** by IR, NMR, and TLC.

Conversion of 3d into 2d. A solution containing **3d** (100 mg), *p*-toluenesulfonic acid (50 mg), and benzene (15 mL) was refluxed for 2 h. The product (41 mg) isolated by chromatography was identified as **2d** by IR, NMR, and TLC.

Photolysis of 1d in the Presence of D_2O. Irradiation of **1d** in CH_3CN containing D_2O was done as described above. The ^1H NMR spectrum of compound **2d** obtained in this experiment did not show the signal at δ 5.67 (vide supra), whereas that of compound **3d** exhibited the signal at δ 5.34 (s, 1 H).

1,4-Dimethyl-2-hydroxy-2-(2,3,3-trimethyl-2-propenyl)-piperazine-3,5,6-trione (8). A solution containing 180 mg of **1a**, 1 mL of 2,3-dimethyl-2-butene, and 50 mL of CH_3CN was irradiated in a Pyrex vessel under argon for 3 h. Solvent was removed in vacuo, and the product was separated by flash chromatography on silica gel. Compound **8** (172 mg, 64%) showed the following: mp 167–168 °C; IR (KBr) 3360 and 1660 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 1.47 (s, 3 H, CH_3), 1.57 (s, 6 H, CH_3), 2.64 and 2.87 (AB q, 2 H, J = 14 Hz, CH_2), 3.06 (s, 3 H, NCH_3), 3.20 (s, 3 H, NCH_3), 3.46 (s, 1 H, OH); ^{13}C NMR (Me_2SO-d_6) δ 19.5 (q), 20.7 (q), 20.8 (q), 27.3 (q), 27.5 (q), 43.7 (t), 86.5 (s), 120.3 (s), 133.4 (s), 152.0 (s), 156.7 (s), 170.3 (s). Anal. Calcd for $C_{12}H_{18}N_2O_4$: C, 56.68; H, 7.13; N, 11.01. Found: C, 56.29; H, 7.01; N, 11.13.

Registry No. **1a**, 35141-14-1; **1b**, 99687-11-3; **1c**, 99687-12-4; **1d**, 99687-13-5; **2b**, 99687-14-6; **2c**, 99687-15-7; **2d**, 99687-17-9; **3c**, 99687-16-8; **3d**, 99687-18-0; **8**, 99687-19-1; *N,N'*-diethyloxamide, 615-84-9; *N,N'*-dipropyloxamide, 14040-77-8; *N,N'*-diisobutyloxamide, 14040-76-7; oxalyl chloride, 79-37-8; 2,3-dimethyl-2-butene, 563-79-1.

(13) Recently, we have reported photocyclization of α-oxoamides which is formally similar to the present cyclization, but the mechanisms of the two reactions are completely different; see ref 5a.

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Unambiguous Preparation of a N_α,N_β Chemodifferentiated α,β-Diaminopropionic Ester through Michael Addition onto a Dehydroalanine Derivative

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2,3-Diaminopropionic acid (1), a simple but not a common amino acid, can be found as a constituent of several bioactive natural products such as tuberactinomycin,[1] bleomycins,[2] quisqualic acid,[3] edeine,[4] α- and β-*N*-oxalyl-L-α,β-diaminopropionic acids[5,6] or antibiotic A 19009.[7]

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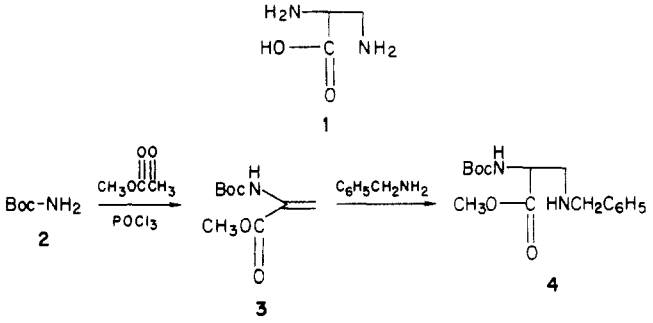
It had been indeed recognized some time ago[8] that among ω-amino amino acids, 1 was a special case: no selective acylation of nitrogen can be performed thus leading to a mixture of products. In order to overcome this difficulty a number of procedures have been proposed,[9-16] but although most of them are efficient they relay on indirect multistep routes. It should be underlined however that they yield optically active material; these procedures are of special interest for syntheses of β-lactams in general[17] and of monobactams in particular[18] for which 1 can be viewed as a convenient building block.[19,20]

We now report hereby a straightforward access to a derivative of 1 having orthogonally protected amino groups, however, under racemic form, via Michael addition of a nitrogen nucleophile to a dehydroalanine moiety. The latter was viewed as an enamine derived from pyruvic acid methyl ester. While reacting carbamic acid *tert*-butyl ester (Boc-NH_2, 2) with methyl pyruvate failed under a number of standard enamine formation conditions, a low yield of the desired product 3 could nevertheless be obtained with titanium tetrachloride as an acidic water scavenger.[21] This result could be improved so as to attain a practical preparative level by use of phosphorus oxychloride as the dehydrating agent. It should be noted that those conditions were reported to fail in this very case[22] but our adjustment of the reaction (3-fold excess of amine 2 for a short time) could lead to a 44–55% isolated yield of 3. This dehydroalanine was readily identified by characteristic olefinic resonances (δ 5.75 and 6.15) in its ^1H NMR spectrum. This route is clearly superior to the recently described three-step procedure which starts with Boc-serine and yields Boc-dehydroalanine benzyl ester.[23]



With regard to the introduction of a second amino group, Michael addition of nitrogen nucleophiles to dehydroalanines appears to have little precedent.[24] Nucleophiles that are precursors of primary amines such as sodium azide or potassium phthalimide could not be reacted with 3; however, when reacted in excess, benzylamine afforded easily the desired compound 4 in 64% yield. Thus only two steps from commercially available starting materials are necessary for the preparation of this 2,3-diaminopropionic acid derivative. The rapidity of the scheme balances the rather fair (~30%) overall yield. It should be underlined as well that the choice of the protecting groups of 4 cannot be varied with this scheme: although a number of protected dehydroalanines are available,[25] the second step appears to be restricted to the use of benzylamine or similar nucleophiles.[26] However as the (*tert*-butyloxy)carbonyl and benzyl groups can be independently deprotected (i.e., they are orthogonal) it is believed that 4 will prove to be a useful synthon.[27]

IR spectra were obtained with a Perkin-Elmer 157 G spectrophotometer. NMR spectra were recorded in $CDCl_3$ on a Bruker WP-80 apparatus; chemical shifts are expressed downfield from Me_4Si in ppm and coupling constants are given in hertz. Mass spectra were obtained with MS 30 or MS 50 Kratos spectrometers.

Experimental Section

***N*-[(*tert*-Butyloxy)carbonyl]dehydroalanine Methyl Ester (3).** Methyl pyruvate (2.042 g, 20 mM) was diluted with benzene (70 mL), and *tert*-butyl carbamate (9.372 g, 80 mM) was added to the solution. It was necessary to heat up the resulting suspension to obtain full dissolution. The flask was then placed at 70 °C, and phosphorus oxychloride (12.27 g, 7.33 mL, 80 mM) was added dropwise within 1 min. After 2 min a heavy white precipitate appeared and the reaction mixture was stirred at 70 °C for a further 15 min. It was then rapidly cooled down and poured into a solution of sodium dihydrogen phosphate (38.4 g, 320 mM) in water (320 mL). The pH was 4, and the aqueous layer was extracted thrice with dichloromethane. The organic layer was washed with water, dried, and evaporated under reduced pressure. Chromatography of the resulting oil was performed on silica gel 60 H (100 g) and elution with dichloromethane afforded 1.89 g (47%) of 3 as a colorless mobile oil. It is advisable to store the product protected from moisture at −10 °C, conditions in which it is stable for months. However no satisfactory elemental analysis nor mass spectral data could be obtained for this enamine. The following data are in agreement with the proposed structure: IR ($CHCl_3$) 3420 (NH), 1715 (br, CO), 1635 cm^{-1} (C=C); ^1H NMR 1.5 (s, 9 H, $(CH_3)_3C$), 3.85 (s, 3 H, $COOCH_3$), 5.75 (d, J = 1.4, 1 H) and 6.15 (s, 1 H) (=CH_2), 7.0 (br, 1 H, NH).

***N*$_\alpha$-[(*tert*-Butyloxy)carbonyl]-*N*$_\beta$-benzyldiaminopropionic Acid Methyl Ester (4).** The preceeding dehydroalanine derivative (0.89 g, 4.43 mM) was diluted with dry (distilled from magnesium) methanol (6 mL) under argon. Benzylamine (1.186 g, 11.07 mM, 1.2 mL) was added via syringe, and the reaction mixture was stirred overnight at 45 °C. Evaporation of methanol and then benzylamine under vacuum was performed and chromatography on silica gel 60 afforded 4 by elution with ethyl acetate. The yield of this colorless syrupy oil was 0.87 g (64%). Anal ($C_{16}H_{24}N_2O_4$) Calcd: C, 62.31; H, 7.84; N, 9.09. Found: C, 62.26; H, 7.76; N, 9.10. Exact mass for $C_{12}H_{14}N_2O_3$ [(M − $(CH_3)_3COH)^+$] calcd 234.1001, found 234.1004; IR ($CHCl_3$) 3430 (NH), 1735 and 1705 cm^{-1} (CO); ^1H NMR 1.45 (s, 9 H, $(CH_3)_3C$), 3.0 (d, J = 5.1, 2 H, $CHCH_2N$], 3.75 (s, 3 H, OCH_3), 3.8 (almost A_2 system, 2 H, $NCH_2C_6H_5$), 4.4 (m, 1 H, CH), 5.4 (d, J = 7, 1

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H, NH), 7.3 (s, 5 H, C_6H_5); ^{13}C NMR 28.2 (q, $C(CH_3)_3$), 50.0 (t, $CHCH_2$), 52.2 (q, OCH_3), 53.4 (t, $NCH_2C_6H_5$), 53.8 (d, $CHCH_2$), 79.9 (s, $C(CH_3)_3$), [aromatic carbons at] 127.0 (para), 128.0 (ortho), 128.4 (meta), 140.0 (ipso), 155.4 (s, NCOO), 172.4 (s, $COOCH_3$), MS (70 eV) *m/e* 234, 175, 149, 132, 120, 91 (100), 77, 65, 57, 51, 41.

Registry No. 2, 4248-19-5; 3, 55477-80-0; 4, 99532-92-0; $C_6H_5CH_2NH_2$, 100-46-9; methyl pyruvate, 600-22-6.

Synthesis and Properties of the Cyclohexa[*cd*]perylenium Tetrafluoroborate. A Homologue of the Phenalenium Ion

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The odd-alternant phenalenyl system **1** has intrigued both experimental and theoretical chemists due to its unique electronic structure.[1] Although there is much current interest in the species consisting of the phenalenyl system,[2] little is known for the extended odd-alternant systems related to **1**.[3] Cyclohexa[*cd*]perylenyl system (**2**), in which two phenalenyl skeletons share their active (starred) sites of 1,3-positions on the one hand and of 1,9-positions on the other, can be regarded as a higher homologue of **1** from various points of view. First, both **1** and **2** are odd-alternant hydrocarbons. Second, simple Hückel molecular orbital theory predicts that **2** has 1 nonbonding and 11 bonding molecular orbitals with the energies given in Figure 1. The cyclohexa[*cd*]perylenium ion (2^+) thus possesses 22 π-electrons which exactly fill pairwise the 11 bonding molecular orbitals. The additional one or two electrons of the radical ($2^{\cdot}$) or the anion (2^-) occupy the nonbonding molecular orbital. Hence all three species should possess the same magnitude of π-electron energy and also the same delocalization energy. Third, the charge density distribution in 2^+ and 2^- are found at positions 1, 3, 4, 5a, 6, 8, 9, 11, 11b, and 13 (starred atoms) and zero at the remaining positions (unstarred atoms). The central carbon atoms, C_α and C_β (see Figure 1), have no charge since the nonbonding MO coefficients at these atoms vanish, even though these are starred atoms. In connection with our study on the phenalenyl system we now report the synthesis and some properties of 2^+.

Knoevenagel reaction of 3-perylenecarboxaldehyde (**3**),[4] obtained from perylene with phosphoryl chloride and

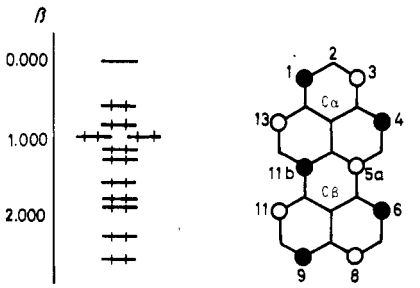


Figure 1. Hückel molecular orbital energies and nonbonding MO coefficients of **2**.

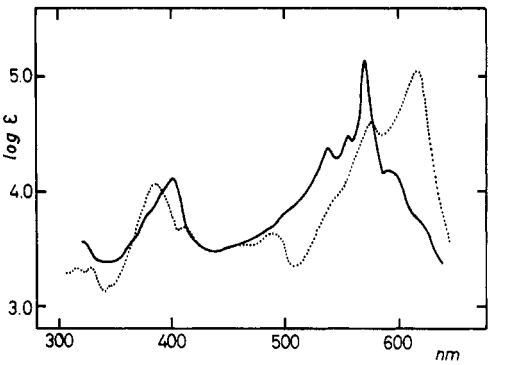
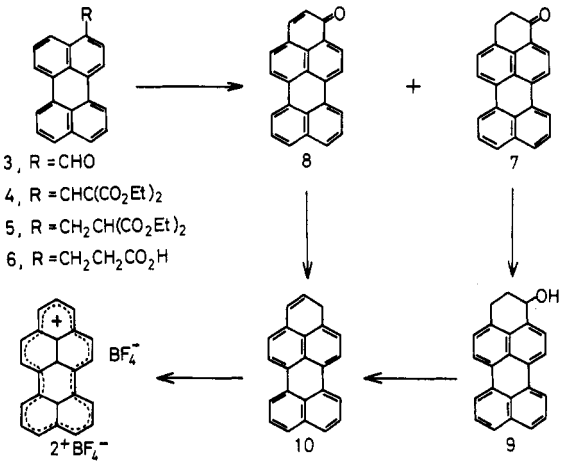


Figure 2. UV-vis spectra of 2^+(—) and **8** (···) in CF_3COOH.

N-methylformanilide in 94% yield with diethyl malonate led to 76% yield of α,β-unsaturated diester **4**, mp 206 °C. Reduction of **4** by zinc–acetic acid yielded **5** in 92% yield.



On hydrolysis and subsequent decarboxylation of **5**, β-(3-perylenyl)propionic acid (**6**), mp 273 °C, was obtained in almost quantitative yield. Treatment of **6** with phosphorous pentachloride in benzene under reflux followed by treatment with anhydrous tin(IV) chloride at 5~10 °C for 1 h gave **7** (42%), orange prisms, mp 185 °C, and **8** (8%), violet powder, mp >300 °C. **8** was also obtained from **7** by dehydrogenation with DDQ in benzene. Reduction of **7** with $NaBH_4$ gave the alcohol **9** in 85% yield, yellow powder, mp 170~5 °C. The hydrocarbon **10**, a common potential precursor to 2^+, $2^{\cdot}$, and 2^-, was derived from **9** with β-naphthalenesulfonic acid in benzene or from **8** by reduction with DIBAL-H. However, **10** could not be isolated in pure form due to its pronouced sensitivity toward air and heat. Hydride abstraction from the freshly prepared crude hydrocarbon **10** with triphenylmethyl tetrafloroborate in dichloromethane at room temperature immediately gave the desired cation salt ($2^+\mathbf{BF_4^-}$) as a deep red powder, mp > 300 °C, which can be stored without any change under atmospheric conditions.

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