Supporting Information to

Syntheses of Novel 1,3-Diazaazulene Derivatives And Their Nonlinear Optical Characterization

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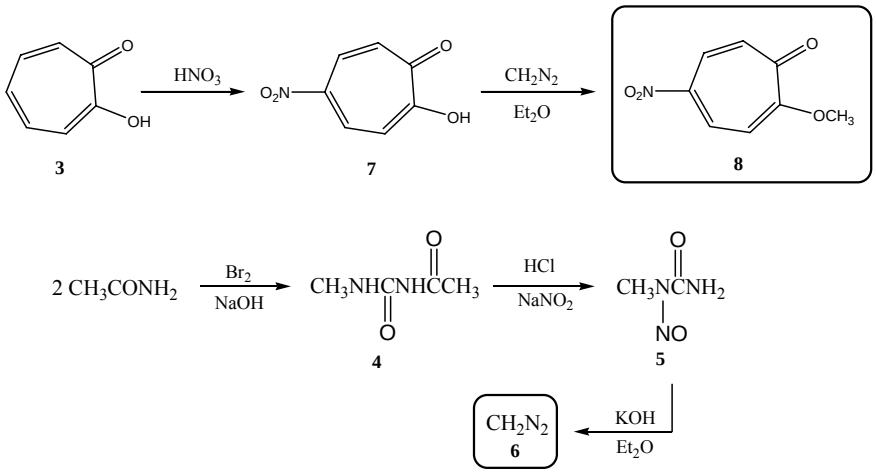
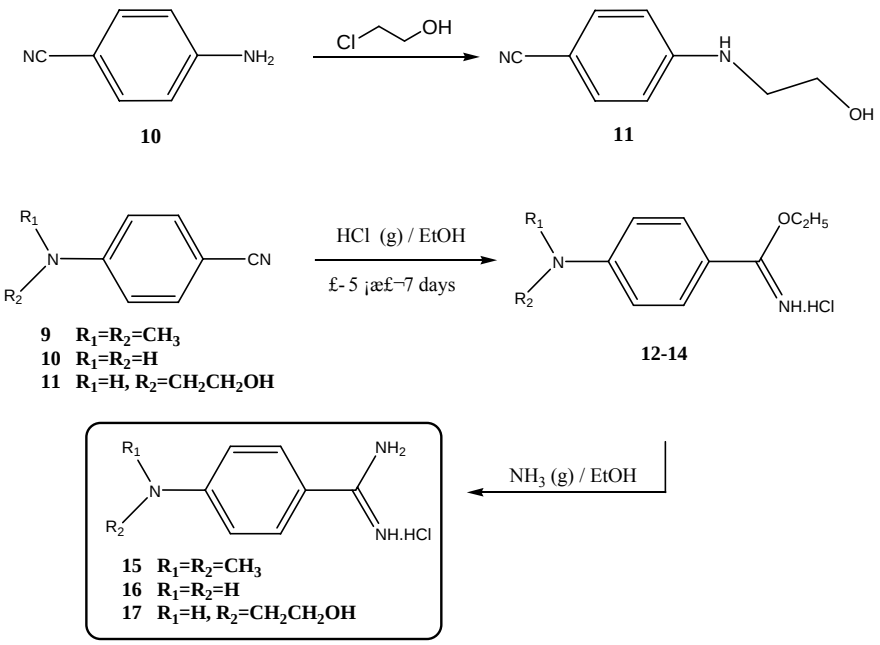
1. Syntheses of starting materials 1~17





Scheme S1. Synthetic routes of the precursors **8**, **15**~**17** for the novel 1,3-diazaazulene derivatives (**18**~**20**)

1.1 Preparation of tropolone

*Decomposition of cyclopentadiene (**1**).* Cyclopentadiene, commercial dimer, must be degraded in the form of monomer before use. Dimeric cyclopentadiene (100 ml) was poured into the round bottom flask (250 ml) with fractionation column, and heated with an oil bath at the temperature of 140~150 °C. When gas evolution was observed, the fraction at 40~45 °C was collected and cooled with an ice bath. The monomeric cyclopentadiene (**1**) totaled about 60 ml and should be used for the next reaction immediately or frozen to avoid redimerization again.

*Preparation of 7,7-dichlorobicyclo[3,2,0]hepta-2-ene-6-ketone (**2**).* Under nitrogen protection, to a solution of dichloracetyl chloride (34 g, 0.23 mol) and cyclopentadiene (**1**) (60 ml, 0.7 mol) in pentane (230 ml), heated to reflux in a

three-necked flask with constant pressure funnel and condenser tube, was added dropwise via funnel triethylamine (24 g, 0.24 mol) in pentane (100 ml) with mechanical stirring during 4 hours, and a lot of white triethylamine hydrochloride was produced. After reflux for 2 hours, water (80 ml) was added to dissolve the triethylamine hydrochloride. The reaction mixture was extracted with pentane (2 × 60 ml). The combined extracts were filtered and dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give brownish black oil. Fraction of reduced pressure distillation at 83~87 °C/400 Pa was collected to give product (**2**, 33.5 g) as a colorless oil. The spectral data of this sample were as follows: n_D^{25} = 1.5129; IR 1806 cm^{-1} (C=O), 1608 cm^{-1} (C=C); ^1H NMR (200 MHz, $CDCl_3$) δ 2.70 (m, 2H, CH_2), 4.10 (m, 2H, 2CH), 5.90 (m, 2H, CH=CH).

*Preparation of tropolone (**3**).* To a mixture of sodium hydroxide (33 g) with glacial acetic acid (270 ml) was added dropwise via funnel **2** (33.5 g) under nitrogen, and the mixture was heated to reflux for 8 hours. After PH was adjusted to 1 with hydrochloric acid (50 ml), the mixture was filtered and extracted with benzene (3 × 90 ml). The combined extracts were concentrated *in vacuo* to give brownish black oil. Fraction of reduced pressure distillation at 100 °C/67 Pa was collected to give gross product (**3**, 22 g) as a pale yellow solid. Recrystallization from mixture of dichloromethane and pentane (1/4, V/V) gave analytically pure product **3** (17.8 g, 77%) as a white needle crystal, m.p. 50~51 °C. The spectral data were as follows: IR 3210 cm^{-1} (OH), 1613 cm^{-1} (C=O), 1548 cm^{-1} (C=C); ^1H NMR (200 MHz, $CDCl_3$) δ 8.8 (s, 1H, OH), 7.33 (m, 5H, 5CH).

1.2 Preparation of diazomethane

Diazomethane was used without further purification in the synthesis of the 2-methoxy-5- nitrotropone (*vide infra*).

*Preparation of acetyl methylurea (**4**).* To a solution of acetamide (15 g, 0.25 mol) in bromine (22 g), warmed slowly with stirring, was added dropwise via syringe sodium hydroxide (10 g, 0.25 mol) in water (25 ml). The mixture was heated to bubble up. After 3 minutes additional heating, the reaction mixture was cooled down with ice bath, filtered and washed with ice water (3 × 10 ml) to give acetyl methylurea (**4**, 12 g) as a white powder, which was used without further purification.

*Preparation of α-nitroso-α-methylurea (**5**).* A mixture of **4** (12 g) and hydrochloric acid (63%, 12 ml) was heated to 100 °C. After additional heating for 4 minutes, water (15 ml) was added, and the mixture was cooled with ice bath below 10 °C. A solution of sodium nitrite (9.5 g) in ice water (14 ml) was added dropwise via funnel with stirring. The reaction mixture was cooled with ice bath and filtered to give *α*-nitroso-*α*-methylurea (**5**, ~8 g) as a pale yellow solid.

*Preparation of diazomethane (**6**).* To a solution of potassium hydroxide (30 mL, 40%) in ether (100 ml), cooled below 5 °C with ice bath, was added in batches **5** with stirring. The organic phase was separated and dried over globosity potassium hydroxide for 3 hours. There is diazomethane (**6**, ~2.6 g) in the ether solution, which was used without further purification.

1.3 Preparation of 2-methoxy-5-nitrotropone

*Preparation of 5-nitrotropolone (**7**).* A solution of tropolone (1.0 g) in water (40 ml), cooled below 15 °C with ice bath, was added dropwise via funnel nitric acid (40 ml, 50%) with stirring. After additional stirring for 5 minutes, the reaction mixture was filtered and recrystallization from pure acetonitrile gave 0.35 g (26%) of analytically pure 5-nitrotropolone (**7**) as a yellow needle crystal, m.p. 195~197 °C. IR 3200 cm^{-1} (OH), 1605 cm^{-1} (C=O), 1540 cm^{-1}, 1320 cm^{-1} (NO_2); MS 167 (M^+); ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 8.56 (d, 2H, 2CH), 7.33 (d, 2H, 2CH). Anal. Calcd. For $C_7H_5NO_4$: C, 50.30; H, 2.99; N, 8.38. Found: C, 50.28; H, 2.99; N, 7.92.

*Preparation of 2-methoxy-5-nitrotropone (**8**).* To a solution of **7** (0.73 g) in ethylene glycol dimethyl ether (25 ml) was added in batches diazomethane in ether with stirring for 12 hours. The reaction mixture was filtered, and recrystallization from pure methanol gave 0.46 g (58%) of analytically pure 2-methoxy-5-nitrotropone **(8)** as a yellow needle crystal, m.p. 160 °C (sublimation). IR 2920 cm^{-1} (OH), 1650 cm^{-1} (C=O), 1560 cm^{-1}, 1360cm^{-1} (NO_2); MS 181 (M^+); ^1H NMR (200 MHz, $CDCl_3$) δ (ppm) 8.45 (q, 1H, CH), 8.15 (q, 1H, CH), 7.13 (q, 1H, CH), 7.10 (q, 1H, CH), 4.01 (s, 3H, CH_3). Anal. Calcd. For $C_8H_{57}NO_4$: C, 53.04; H, 3.87; N, 7.73. Found: C, 52.66; H, 3.89; N, 7.66.

1.4 Preparation of 4-substitued aminobenzamidine hydrochloride

4-*N*,*N*-Dimethylaminobenzonitrile (**9**) and 4-aminobenzonitrile (**10**) were commercial and used without further purification.

*Preparation of 4-(N-2'-ethoxyl)-aminobenzonitrile (**11**).* A solution of

4-aminobenzonitrile (**10**) (12 g, 0.102 mol) and 2-chlorethanol (12 ml, 0.179 mol) in absolute methanol (40 ml) was heated to reflux with stirring under nitrogen for 24 hours. The mixture was concentrated *in vacuo* to give yellow oil. Standard silica gel (~200 mesh) column chromatography eluting with mixture of chloroform and ethyl acetate (2/1, V/V) and recrystallization from pure ethanol gave 4.8 g (30%) of 4-(*N*-2'-ethoxyl)-aminobenzonitrile (**11**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, J = 8.43 Hz, 2H, CH), 6.60 (d, J = 8.43 Hz, 2H, CH), 3.88 (s, 2H, CH_2), 3.34 (s, 2H, CH_2); MS 162 (M^+).

*Preparation of 4-(N,N-dimethylaminophenyl) ethyl imino ether hydrochloride (**12**).* To a solution of 4-*N*,*N*-dimethylaminobenzonitrile (**9**) (4.8 g, 0.03 mol) in ethanol (50 ml), cooled to −30 °C, was added hydrochloric acid gas with stirring for 12 hours. The reaction mixture was dried over anhydrous $CaCl_2$, cooled at −5 °C, and filtered to give 3.8 g (66%) of 4-(*N,N*-dimethylaminophenyl)ethyl imino ether hydrochloride (**12**) as a yellow powder. ^{1}H NMR (300 MHz, D_2O) δ 7.89 (d, 2H, J = 8.9 Hz), 7.10 (d, 2H, J = 8.9 Hz), 4.48 (q, J = 7.0 Hz, 2H, CH_2), 3.08 (6H, s), 1.28 (t, 3H, J = 7.0 Hz, CH_3); MS 193.1 (M^+ + 1).

*Preparation of 4-aminophenyl ethyl imino ether hydrochloride (**13**).* The procedure was similar to that for **12**. To a solution of 4-aminobenzonitrile (**10**) (4.5 g, 0.03 mol) in ethanol (50 ml), cooled to −30 °C, was added dry hydrochloride gas with stirring for 12 hours. The reaction mixture was dried over anhydrous $CaCl_2$, cooled at −5 °C, and filtered to give 3.0 g (60%) 4-aminophenyl ethyl imino ether hydrochloride (**13**) as a yellow powder. ^{1}H NMR (300 MHz, D_2O) δ 7.48 (d, J = 8.0

Hz, 2H, 2CH), 6.67 (d, J = 8.0 Hz, 2H, 2CH), 4.42 (q, J = 6.8 Hz, 2H, CH_2), 1.46 (t, J = 6.8 Hz, 3H, CH_3); MS 165.1 (M^+ + 1).

*Preparation of 4-(N-2'-ethoxylaminophenyl) ethyl imino ether hydrochloride (**14**).* The procedure was similar to that for **12**. To a solution of 4-(*N*-2'-ethoxyl)-aminobenzonitrile (**11**) (5.0 g, 0.03 mol) in ethanol (50 ml), cooled to −30 °C, was added dry hydrochloride with stirring for 12 hours. The reaction mixture was dried over anhydrous $CaCl_2$, cooled at −5 °C, and filtered to give 3.1 g (50%) 4-aminophenyl ethyl imino ether hydrochloride (**14**) as a yellow powder. ^{1}H NMR (400 MHz, CD_3OD) δ 7.75 (d, J = 8.0 Hz, 2H, 2CH), 6.82 (d, J = 8.0 Hz, 2H, 2CH), 4.44 (q, J = 6.9 Hz, 2H, CH_2), 3.72 (t, J = 5.4 Hz, 2H, CH_2), 3.35 (t, J = 5.4 Hz, 2H, CH_2), 1.47 (t, J = 6.9 Hz, 3H, CH_3); MS 209.1 (M^+ + 1).

*Preparation of 4-(N,N-dimethylamino) benzamidine hydrochloride (**15**).* **12** (3.8 g) was added to a solution of ammonia (12 g) in ethanol (150 ml, ~8% mass percent) with stirring at room temperature for 24 hours. The reaction mixture was filtered and concentrated *in vacuo*, and acidated with hydrochloric acid (5 ml, 63%). Absorbent charcoal was used to purify. The mixture was filtered, and concentrated and dried *in vacuo* at room temperature to give 5.6 g (84%) of 4-(*N,N*-dimethylamino) benzamidine hydrochloride (**15**) as a bright yellow solid. ^{1}H NMR (300 MHz, d_6-DMSO) δ 9.02 (1H, s/br), 8.81 (1H, s/br), 7.78 (2H, d, J = 8.9 Hz), 6.80 (2H, d, J = 8.9 Hz), 3.01 (6H, s); MS 222.1 (M^+ + 1).

*Preparation of 4-aminobenzamidine hydrochloride (**16**).* The procedure was similar to that for **15**. **13** (3.0 g) was added to a solution of ammonia (12 g) in ethanol

(150 ml, ~8% mass percent) with stirring at room temperature for 24 hours. 5.0 g (86%) of 4-aminobenzamidine hydrochloride (**16**) was obtained as a bright yellow solid. ^{1}H NMR (300 MHz, D_2O) δ 7.58 (d, J = 8.3 Hz, 2H, 2CH), 6.77 (d, J = 5.5 Hz, 2H, 2CH); MS 136.1 (M^+ + 1).

*Preparation of 4-(N-2'-ethoxylamino) benzamidine hydrochloride (**17**).* The procedure was similar to that for **15**. **14** (3.1 g) was added to a solution of ammonia (12 g) in ethanol (150 ml, ~8% mass percent) with stirring at room temperature for 24 hours. 5.0 g (86%) of 4-(*N,N*-dimethylamino) benzamidine hydrochloride (**17**) was obtained as a bright yellow solid. ^{1}H NMR (400 MHz, CD_3OD) δ 7.65 (d, J = 8.9 Hz, 2H, 2CH), 6.77 (d, J = 8.9 Hz, 2H, 2CH), 3.75 (t, J = 5.8 Hz, 2H, CH_2), 3.35 (t, J = 5.8 Hz, 2H, CH_2); MS 180.1 (M^+ + 1).

2. Instrumentation for HRS and SHG measurements

The hyper-Rayleigh scatting (HRS) setup for the β determination was built according to *refs*. [1, 2] with minor modifications. Briefly, the fundamental wave from a Q-switched Nd^{3+}: YAG laser (1064 nm, 10 ns, ≤15 mJ, 10 Hz) was focused into a cylindrical sample cell by a lens (focal length, 100 mm). The HRS signal at 532 nm, after passing through an interference filter with a center wavelength of 532 nm, was detected with a photomultiplier tube (PMT), and then digitized and averaged by the use of an analogy-to-digital device in a personal computer.

The setups for corona poling at elevated temperature and for *in-situ* SHG

measurement were described in details elsewhere.[3] Briefly, the film was poled in a thermostatic oven with two optical windows and three needle electrodes. The film was laid with a 45° angle with respect to the incident beam and 0.8 cm away from the electrode points. A Y-cut quartz crystal was used as a reference. The SHG signal was detected through an optical widow with a PMT. The SHG coefficient d_{33} was deduced by comparing the intensities of the SHG signal from poled film with that from the quartz crystal. The dependence of the poling-induced orientation stability on temperature, i.e. the depoling curve of the poled film, was also determined with this apparatus.

References

[1] K. Clays, A. Persoons, *Phys. Rev. Lett.* **1991**, *66*, 2980.

[2] K. Clays, A. Persoons, *Rev. Sci. Instrum.* **1992**, *63*, 3285.

[3] P. Zhu, P. Wang, W. Wu, C. Ye, J. *Nonlinear Opt. Phys. Mater.* **1999**, *8*, 461.