# A Chiral 2-D Donor-Acceptor Array of a Bipyrazine N-Oxide and Tetracyanoethylene

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**General Methods and Materials.**  All starting materials were purchased from Aldrich.  NMR spectra were obtained using a Bruker AM-360 spectrometer operated at 360 MHz for ^{1}H NMR and 90 MHz for ^{13}C NMR.  Chemical shifts ($\delta$) are reported relative to TMS.  Melting points were determined with a Mel-Temp apparatus and are uncorrected.  IR spectra were recorded on a Avatar 360 FT-IR spectrometer.  UV-vis data were recorded on a Hewlett-Packard 8452A diode array spectrometer and GC/MS data were obtained using a Hewlett-Packard 5890/5971 GC/MS instrument with a fused silica capillary column (25m) of cross-linked methylsilicone and operating in EI mode at 70 eV ionizing voltage.

Acetonitrile (Fisher, HPLC grade) was purified by distillation from $P_2O_5$. Dichloromethane (Fisher, reagent grade) was stirred over concentrated $H_2SO_4$ until the acid layer ceased to darken further, washed with aq $Na_2CO_3$ and $H_2O$, dried with anhydrous $CaCl_2$, and then distilled from $CaH_2$.  Tetrahydrofuran (Fisher, HPLC grade) was refluxed with K metal and benzophenone and distilled upon establishment of a dark blue solution.  TCNE was purified by multiple sublimations at 0.05 mm Hg at 90-100 ˚C through a bed of activated charcoal until perfectly colorless cubic crystals were obtained.

The powder diffraction spectra were collected on a Rigaku Geigerflex powder diffractometer (Cu K$\alpha$ radiation ) using 1° slits with scan conditions as follows: scan speed 0.125 - 0.150 ˚/min, sampling interval 0.050˚, 2$\Theta$ range 5.00 - 40.00˚.  A Siemens SMART diffractometer equipped with CCD area detector using graphite monochromated Mo K$\alpha$ radiation was used to collect data for all single crystal structures.  Crystals analyzed were mounted on glass

fibers using grease and data were collected at -100 ˚C. Solution and refinement of the data was performed using the SHELXTL[1] crystallographic software package. All non-hydrogen atoms were refined anisotropically.

**2-(1H)-3,5,6-Trimethylpyrazinone (3)** was prepared according to literature procedures.[2,3]

**2-Chloro-3,5,6-trimethylpyrazine (4).**[2] In a 100 mL round bottom flask equipped with a reflux condenser was placed **3** (1.9975 g, 0.014475 mol), $POCl_3$ (11 mL, 0.12 mol), and one drop of concentrated sulfuric acid. The mixture was refluxed under nitrogen for 20 hours. After allowing the mixture to cool to 25 ˚C, 40 mL of ether was added followed by 72 g of ice to effect hydrolysis of excess $POCl_3$. While cooled in an ice bath, the mixture was basified to a pH > 10 with 50% KOH solution. The mixture was then continuously extracted with ether for 14 days. After removal of the ether *in vacuo*, the resulting crude product was loaded onto a column of grade 1 basic alumina (l x w = 5.5 cm × 5.1 cm). Elution with $CH_2Cl_2$ gave pure **4**, 1.0405 g (45.90%): mp 50-51 °C (lit.[2] 56-57 °C). ^{1}H NMR (360 MHz, $CDCl_3$) δ 2.57 (s, 3H), 2.48 (s, 6H).

**3,3´,5,5´,6,6´-Hexamethyl-2,2´-bipyrazine (5).** This procedure was adapted from that of Constable et al..[4] Following the procedure of Perrin and Armarego,[5] 10 g of zinc dust (Aldrich) was activated by stirring it a 150 mL beaker with 25 mL of 2% HCl for one minute. The acid was removed by filtration and the zinc was then washed with 2 x 25 mL of 2% HCl, 3 x 8 mL of distilled water, 2 x 17 mL of 95% EtOH, and 2 x 17 mL of anhyd ether. The zinc was then thoroughly dried in *vacuo* and stored under $N_2$ until use. In a 50 mL two-necked round bottom flask was placed acid washed zinc (0.6724 g, 10.29 mmol), tetramethylammonium iodide (1.7140 g, 6.665 mmol), triphenylphosphine (1.0287 g, 3.922 mmol), $NiCl_2$ (0.2694 g, 2.078 mmol), and dry THF (40 mL) purged with $N_2$. The mixture was stirred under $N_2$ for approximately 50 min until a red-brown color was observed. At this time, **4** (1.0405 g, 6.644 mmol), dissolved in 20 mL of dry THF, was added via syringe and the mixture was stirred at 45-50 °C for 7 days.

The mixture was then cooled to room temperature and 2M $NH_4OH$ was added until a pH > 10 was achieved. The reaction mixture was then filtered through a cotton plug and extracted with ethyl acetate (6 × 25 mL). The combined organic layers were concentrated by evaporation *in vacuo* and extracted with 2M HCl (5 × 5 mL). The combined aqueous layers were made basic (pH > 10) while cooled in an ice bath by addition of KOH pellets. The basic aqueous solution was then extracted with ethyl acetate (5 × 10 mL). Following removal of the ethyl acetate *in vacuo*, the resulting crude product was purified by column chromatography (silica gel, l x w = 13.1 cm × 4.0 cm). Elution with ethyl acetate gave a pure white, crystalline solid, **5**, 0.5638 g, (70.13%): mp 122 °C. $^1H$ NMR (360 MHz, $CDCl_3$) δ 2.58 (s, 6H), 2.55 (s, 6H), 2.35 (s, 6H); $^{13}C$ NMR (90 MHz, $CDCl_3$) δ 151.28, 148.92, 148.47, 147.67, 21.86, 21.54, 21.10; IR (KBr, $cm^{-1}$) 2990, 2948, 2923, 1446, 1401, 1384, 1363; HRMS (EI) calcd. for $C_{14}H_{18}N_4$ ($M^+$) 242.1532, found 242.1538.

**3,3´,5,5´,6,6´-Hexamethyl-2,2´-bipyrazine-N,N´,N´´,N´´´-tetraoxide (1).**[6] In a 50 mL round bottom flask was placed OXONE® (0.5007 g, 814.4 μmol) dissolved in approximately 2 mL of water. To this was added **5** (49.0 mg, 202 μmol) dissolved in 1 mL of $CH_2Cl_2$ and the biphasic solution stirred vigorously. Over the course of 5 days another 0.9982 g (162.4 μmol) of OXONE® was added to force the reaction to completion. After the initial five days, the reaction mixture was refluxed for another five days at 45 - 50 °C, again to force the reaction toward complete oxygenation. The organic layer of the reaction mixture was then isolated and the aqueous layer extracted with $CH_2Cl_2$ (5 × 10 mL). After removal of the $CH_2Cl_2$ *in vacuo*, the crude solid (~ 0.2 g) was purified on silica gel prep plates (0.1 g per 250 μm coated plate). Elution with $CH_2Cl_2$/MeOH (10:1, $R_f = 0.3$) gave a colorless crystalline solid, **1**, 56.3 mg (90.9 %): mp 267-275 °C (dec.). $^1H$ NMR (360 MHz, $CDCl_3$) δ 2.63 (s, 6H), 2.58 (s, 6H), 2.32 (s, 6H); $^{13}C$ NMR (90 MHz, $CDCl_3$) δ 145.99, 144.43, 143.71, 134.71, 14.74, 14.40, 14.06; IR (KBr, $cm^{-1}$) 2927, 1509, 1437, 1311, 1289, 1103; HRMS (EI) calcd. for $C_{14}H_{18}N_4O_4$ ($M^+$) 306.1328, found 306.1336.

**Crystallization of 1(TCNE)$_2$.** In a 5 mL vial, **1** (5.0 mg, .016 mmol) and TCNE (5.1 mg, .040 mmol) were dissolved in 0.4 mL of $CH_2Cl_2$ along with a few drops of ether. The vial was then placed in a closed ether chamber and cooled in a freezer to -20 °C. After 6 days, red, cube-shaped crystals were collected: mp 165 °C (dec.).

**JOB Plot Analysis.** A JOB plot of the **1**/TCNE complex absorbance vs. mole fraction TCNE was prepared from UV-vis results in $CH_2Cl_2$ at 25 °C with [**1**] + [TCNE] = 0.020 M. Spectra were recorded at TCNE mole fractions of 10, 20, 30, 40, 50, 60, 70, 80, and 90% to give CT absorbances (496 nm - 800 nm) of 0.4978, 0.8408, 1.0847, 1.2653, 1.3069, 1.2441, 1.1248, 0.8776, 0.4815, respectively.

**Benesi-Hildebrand Analysis.** Benesi-Hildebrand analysis of **1**/TCNE complexation was performed in $CH_2Cl_2$ at 25 °C using [**1**] = 0.00118 M and [TCNE] = 0.0111, 0.0200, 0.0301, 0.0398, 0.0486, and 0.0584 M. Plots of 1/[TCNE] vs. [**1**]/Abs were prepared from UV-vis data at 480, 490, 500, 510, and 520 nm. CT absorbance values were corrected for baseline drift by subtraction of absorbance at 800 nm. The average $K_f$ value was found to be 3.59 $M^{-1}$ ± 0.1. Standard deviation was calculated using a T-value correction factor at confidence levels of 95%.[7]

**Table 1.  Data for Benesi-Hildebrand Study of 1/TCNE in $CH_2Cl_2$ at 25 ˚C**

| **1** (mM) | TCNE (mM) | $A_{480-800}$ | $A_{490-800}$ | $A_{500-800}$ | $A_{510-800}$ | $A_{520-800}$ |
|---|---|---|---|---|---|---|
| 1.18 | 11.1 | 0.17882 | 0.18480 | 0.18538 | 0.17950 | 0.16893 |
| 1.18 | 19.9 | 0.29792 | 0.30890 | 0.30986 | 0.30060 | 0.28245 |
| 1.18 | 30.1 | 0.42659 | 0.44380 | 0.44618 | 0.43280 | 0.40590 |
| 1.18 | 39.8 | 0.55632 | 0.57830 | 0.58101 | 0.56260 | 0.52787 |
| 1.18 | 48.6 | 0.66085 | 0.68740 | 0.69048 | 0.66820 | 0.62633 |
| 1.18 | 58.4 | 0.77722 | 0.80860 | 0.81136 | 0.78440 | 0.73399 |
| $\varepsilon$ ($M^{-1}cm^{-1}$) | | 4373 | 4686 | 4777 | 4492 | 4092 |
| $K_f$ ($M^{-1}$) | | 3.65 | 3.53 | 3.47 | 3.59 | 3.88 |
| $r^2$ | | 0.999 | 0.999 | 1.000 | 1.000 | 1.000 |

**X-ray Powder Diffraction and X-ray Single Crystal Data Tables**

X-ray powder diffraction spectra were taken of 15-20 mg samples of **1**(TCNE)$_2$ cocrystals. The samples were ground into powder and mounted on a 1cm x 1cm glass slide using double-sided tape.  A calculated powder diffractogram for the observed **1**(TCNE)$_2$ single crystal structure was obtained via the SHELXTL XPOW subroutine.[1]

**Table 2.  Powder Diffraction Results for 1(TCNE)$_2$**

| Sample | Observed (2Θ, deg) | | | Calculated (2Θ, deg) | | |
|---|---|---|---|---|---|---|
| **1**(TCNE)$_2$ | 10.36 | 17.33 | 26.34 | 10.43 | 17.32 | 26.35 |
| | 13.02 | 23.08 | 26.48 | 13.02 | 23.26 | 26.51 |
| | 13.10 | 26.20 | 27.01 | 13.16 | 26.23 | 27.20 |

**Table 3. Crystal Data and Structure Refinement for 1(TCNE)$_2$.**

| | |
|---|---|
| Empirical formula | C26 H18 N12 O4 |
| Formula weight | 562.52 |
| Temperature | 173(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | C2/c |
| Unit cell dimensions | a = 18.1957(6) Å   alpha = 90 deg. |
| | b = 10.06870(10) Å    beta = 118.699(2) deg. |
| | c = 18.1772(6) Å   gamma = 90 deg. |
| Volume, Z | 2921.09(14) Å^3,  4 |
| Density (calculated) | 1.279 Mg/m^3 |
| Absorption coefficient | 0.092 mm^-1 |
| F(000) | 1160 |
| Crystal size | 0.12 x 0.12 x 0.54 mm |
| Theta range for data collection | 2.39 to 25.00 deg. |
| Limiting indices | -22<=h<=23, -12<=k<=13, -23<=l<=10 |
| Reflections collected | 7451 |
| Independent reflections | 2560 [R(int) = 0.0343] |
| Absorption correction | None |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 2522 / 0 / 227 |
| Goodness-of-fit on F^2 | 1.036 |
| Final R indices [I>2sigma(I)] | R1 = 0.0514, wR2 = 0.1074 |
| R indices (all data) | R1 = 0.0875, wR2 = 0.1334 |
| Extinction coefficient | 0.0039(5) |
| Largest diff. peak and hole | 0.465 and -0.173 e.A^-3 |

**Table 4. Atomic Coordinates (x $10^4$) and Equivalent Isotropic Displacement Parameters (Å x $10^3$) for 1(TCNE)$_2$.**
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 5024(1) | 8970(2) | 1625(1) | 32(1) |
| N(2) | 4421(1) | 9753(2) | 1539(1) | 26(1) |
| O(3) | 2609(1) | 12312(2) | 1263(1) | 41(1) |
| C(4) | 4571(1) | 10692(2) | 2137(1) | 24(1) |
| N(5) | 3187(1) | 11468(2) | 1357(1) | 28(1) |
| C(6) | 3650(1) | 9655(2) | 844(1) | 26(1) |
| C(7) | 3960(1) | 11560(2) | 2056(1) | 27(1) |
| C(8) | 4066(2) | 12618(3) | 2667(2) | 42(1) |
| C(9) | 3019(1) | 10505(2) | 763(1) | 28(1) |
| C(10) | 2146(2) | 10482(4) | 57(2) | 42(1) |
| C(11) | 3573(2) | 8633(3) | 222(2) | 38(1) |
| C(12) | 895(2) | 13081(3) | 534(2) | 40(1) |
| N(13) | 590(2) | 13236(3) | −170(2) | 51(1) |
| C(14) | 1278(2) | 12943(3) | 1439(2) | 40(1) |
| C(15) | 463(2) | 10952(3) | 1259(2) | 43(1) |
| C(16) | 1842(2) | 13966(3) | 1963(2) | 43(1) |
| C(17) | 1067(2) | 11951(3) | 1775(2) | 41(1) |
| C(18) | 1398(2) | 11869(3) | 2667(2) | 48(1) |
| N(19) | 2275(2) | 14789(3) | 2365(2) | 69(1) |
| N(20) | −4(2) | 10143(3) | 912(2) | 75(1) |
| N(21) | 1632(2) | 11778(3) | 3366(2) | 78(1) |

**Table 5. Bond Lengths (Å) and Angles (deg) for 1(TCNE)$_2$**

| | |
|---|---|
| O(1)-N(2) | 1.298(2) |
| N(2)-C(6) | 1.368(3) |
| N(2)-C(4) | 1.366(3) |
| O(3)-N(5) | 1.298(2) |
| C(4)-C(7) | 1.365(3) |
| C(4)-C(4) | 1.483(4) |
| N(5)-C(7) | 1.373(3) |
| N(5)-C(9) | 1.371(3) |
| C(6)-C(9) | 1.382(3) |
| C(6)-C(11) | 1.486(3) |
| C(7)-C(8) | 1.482(4) |
| C(9)-C(10) | 1.487(3) |
| C(12)-N(13) | 1.135(3) |
| C(12)-C(14) | 1.452(4) |
| C(14)-C(17) | 1.320(4) |
| C(14)-C(16) | 1.443(4) |
| C(15)-N(20) | 1.126(4) |
| C(15)-C(17) | 1.452(4) |
| C(16)-N(19) | 1.135(3) |
| C(17)-C(18) | 1.436(4) |
| C(18)-N(21) | 1.133(3) |

**Angles (degrees)**

| | |
|---|---|
| O(1)-N(2)-C(6) | 120.0(2) |
| O(1)-N(2)-C(4) | 119.4(2) |
| C(6)-N(2)-C(4) | 120.6(2) |
| C(7)-C(4)-N(2) | 121.1(2) |
| C(7)-C(4)-C(4) | 123.4(2) |
| N(2)-C(4)-C(4) | 115.5(2) |
| O(3)-N(5)-C(7) | 118.9(2) |
| O(3)-N(5)-C(9) | 119.9(2) |
| C(7)-N(5)-C(9) | 121.3(2) |
| N(2)-C(6)-C(9) | 119.0(2) |
| N(2)-C(6)-C(11) | 115.6(2) |
| C(9)-C(6)-C(11) | 125.3(2) |
| C(4)-C(7)-N(5) | 118.4(2) |
| C(4)-C(7)-C(8) | 124.9(2) |
| N(5)-C(7)-C(8) | 116.7(2) |
| N(5)-C(9)-C(6) | 119.6(2) |
| N(5)-C(9)-C(10) | 115.7(2) |
| C(6)-C(9)-C(10) | 124.8(2) |
| N(13)-C(12)-C(14) | 177.5(3) |
| C(17)-C(14)-C(16) | 120.5(3) |
| C(17)-C(14)-C(12) | 120.5(3) |
| C(16)-C(14)-C(12) | 118.8(3) |
| N(20)-C(15)-C(17) | 174.8(3) |
| N(19)-C(16)-C(14) | 178.6(3) |
| C(14)-C(17)-C(18) | 120.6(3) |
| C(14)-C(17)-C(15) | 121.5(2) |
| C(18)-C(17)-C(15) | 117.8(3) |
| N(21)-C(18)-C(17) | 177.3(4) |

s1    SHELXTL/PC Version 5.0 Structure Analysis Package, Siemens Industrial Automation, Inc., 1994.

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