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# Gas-phase formation and spectroscopic characterization of the disubstituted cyclopropenylidenes c-C3(C2H)2, c-C3(CN)2, and c-C3(C2H)(CN)

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# Supplemental Information

Gas-phase formation and spectroscopic characterization of the disubstituted cyclopropenylidenes $c$-$C_3(C_2H)_2$, $c$-$C_3(CN)_2$, and $c$-$C_3(C_2H)(CN)$

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## 1 Fermi Resonances

| | |
|---|---|
| $\nu_7+\nu_4=\nu_1$ | (1) |
| $\nu_{20}+\nu_{14}=\nu_{10}$ | (2) |
| $2\nu_{17}=\nu_{20}+\nu_{16}=\nu_{21}+\nu_{17}=\nu_{11}$ | (3) |
| $\nu_{20}+\nu_{15}=\nu_{12}$ | (4) |
| $2\nu_{18}=2\nu_{19}=\nu_{14}$ | (5) |
| $\nu_{18}+\nu_{17}=\nu_{20}+\nu_{19}=\nu_{15}$ | (6) |
| $2\nu_{18}=2\nu_{19}=\nu_{17}$ | (7) |
| $\nu_7+\nu_3=\nu_2$ | (8) |
| $\nu_8+\nu_7=\nu_3$ | (9) |
| $\nu_8+\nu_6=\nu_{15}+\nu_5=\nu_4$ | (10) |
| $\nu_{11}+\nu_6=\nu_{13}+\nu_7=\nu_{15}+\nu_7=\nu_{17}+\nu_6=\nu_5$ | (11) |
| $2\nu_{11}=2\nu_{12}=\nu_{13}+\nu_8=\nu_{15}+\nu_8=\nu_{17}+\nu_{11}=\nu_6$ | (12) |
| $\nu_{14}+\nu_{13}=\nu_{15}+\nu_{11}=\nu_{15}+\nu_{14}=\nu_{16}+\nu_{12}=\nu_7$ | (13) |
| $\nu_{18}+\nu_{11}=\nu_{18}+\nu_{17}=\nu_{19}+\nu_{16}=\nu_{20}+\nu_{12}=\nu_{21}+\nu_15=\nu_8$ | (14) |
| $\nu_{20}+\nu_{13}=\nu_9$ | (15) |

Table 1: Fermi resonances for $c$-$C_3(C_2H)_2$.

| | |
|---|---|
| $2\nu_5=\nu_7+\nu_3=\nu_1$ | (1) |
| $2\nu_12=2\nu_13=\nu_11$ | (2) |
| $\nu_9+\nu_3=\nu_2$ | (3) |
| $\nu_6+\nu_5=\nu_9+\nu_5=\nu_11+\nu_4=\nu_3$ | (4) |
| $2\nu_7=2\nu_8=\nu_9+\nu_6=\nu_11+\nu_7=\nu_4$ | (5) |
| $\nu_9+\nu_7=\nu_{10}+\nu_8=\nu_5$ | (6) |
| $\nu_{12}+\nu_7=\nu_{12}+\nu_{11}=\nu_{13}+\nu_{10}=\nu_{14}+\nu_8=\nu_{15}+\nu_9=\nu_6$ | (7) |
| $2\nu_12=2\nu_13=\nu_12+\nu_9=\nu_14+\nu_10=\nu_15+\nu_11=\nu_7$ | (8) |
| $\nu_14+\nu_9=\nu_8$ | (9) |
| $\nu_12+\nu_11=\nu_14+\nu_13=\nu_9$ | (10) |

Table 2: Fermi resonances for $c$-$C_3(CN)_2$.

| | |
|---|---|
| $\nu_6+\nu_3=\nu_1$ | (1) |
| $\nu_1 7+\nu_1 2=\nu_1 0$ | (2) |
| $2\nu_1 5=2\nu_1 6=\nu_1 1$ | (3) |
| $\nu_1 5+\nu_1 4=\nu_1 7+\nu_1 6=\nu_1 2$ | (4) |
| $2\nu_1 5=2\nu_1 6=\nu_1 4$ | (5) |
| $2\nu_6=\nu_6+\nu_5=\nu_9+\nu_4=\nu_2$ | (6) |
| $\nu_7+\nu_6=\nu_1 2+\nu_4=\nu_3$ | (7) |
| $\nu_9+\nu_6=\nu_1 1+\nu_6=\nu_1 2+\nu_5=\nu_1 2+\nu_6=\nu_1 4+\nu_6=\nu_4$ | (8) |
| $2\nu_1 0=2\nu_1 1=\nu_9+\nu_7=\nu_1 2+\nu_7=\nu_1 2+\nu_9=\nu_1 2+\nu_1 1=\nu_1 3+\nu_1 0=\nu_1 4+\nu_9=\nu_1 5+\nu_6=\nu_5$ | (9) |
| $2\nu_9=2\nu_1 1=\nu_1 1+\nu_7=\nu_1 2+\nu_7=\nu_1 2+\nu_9=\nu_1 3+\nu_1 0=\nu_1 4+\nu_9=\nu_6$ | (10) |
| $\nu_1 5+\nu_9=\nu_1 5+\nu_1 4=\nu_1 6+\nu_1 3=\nu_1 7+\nu_1 0=\nu_1 8+\nu_1 2=\nu_7$ | (11) |
| $\nu_1 7+\nu_1 1=\nu_8$ | (12) |
| $2\nu_1 4=\nu_1 7+\nu_1 3=\nu_1 8+\nu_1 4=\nu_9$ | (13) |

Table 3: Fermi resonances for $c$-$C_3(C_2H)(CN)$.

## 2 Rotational data

Table 4: Full rotational constants for $c$-$C_3(C_2H)_2$.

| **Constant** | **F12-DZ Value (MHz)** |
|---|---|
| $A_e$ | 7845.3 |
| $B_e$ | 1539.4 |
| $C_e$ | 1287.0 |
| $A_0$ | 7823.0 |
| $B_0$ | 1540.8 |
| $C_0$ | 1285.6 |
| $A_1$ | 7818.1 |
| $B_1$ | 1539.8 |
| $C_1$ | 1284.8 |
| $A_2$ | 7817.8 |
| $B_2$ | 1539.8 |
| $C_2$ | 1284.8 |
| $A_3$ | 7799.6 |
| $B_3$ | 1538.1 |
| $C_3$ | 1283.1 |
| $A_4$ | 7806.2 |
| $B_4$ | 1538.0 |
| $C_4$ | 1283.2 |
| $A_5$ | 7772.5 |
| $B_5$ | 1539.2 |
| $C_5$ | 1283.2 |
| $A_6$ | 7799.5 |
| $B_6$ | 1540.8 |
| $C_6$ | 1284.8 |
| $A_7$ | 7848.2 |
| $B_7$ | 1534.6 |
| $C_7$ | 1281.6 |
| $A_8$ | 7784.8 |
| $B_8$ | 1543.4 |
| $C_8$ | 1286.0 |
| $A_9$ | 7820.1 |
| $B_9$ | 1540.8 |
| $C_9$ | 1285.8 |
| $A_{10}$ | 7828.8 |
| $B_{10}$ | 1540.8 |
| $C_{10}$ | 1285.8 |
| $A_{11}$ | 7884.0 |
| $B_{11}$ | 1534.0 |
| $C_{11}$ | 1282.5 |
| $A_{12}$ | 7830.9 |
| $B_{12}$ | 1541.7 |
| $C_{12}$ | 1286.7 |
| $A_{13}$ | 7810.7 |
| $B_{13}$ | 1542.4 |
| $C_{13}$ | 1286.3 |
| $A_{14}$ | 7812.8 |
| $B_{14}$ | 1542.2 |
| $C_{14}$ | 1286.2 |
| $A_{15}$ | 7797.1 |
| $B_{15}$ | 1543.9 |
| $C_{15}$ | 1286.7 |
| $A_{16}$ | 7801.4 |

| | |
|---|---|
| $B_{16}$ | 1543.7 |
| $C_{16}$ | 1287.7 |
| $A_{17}$ | 7842.4 |
| $B_{17}$ | 1541.7 |
| $C_{17}$ | 1286.2 |
| $A_{18}$ | 7838.5 |
| $B_{18}$ | 1543.2 |
| $C_{18}$ | 1287.1 |
| $A_{19}$ | 7818.5 |
| $B_{19}$ | 1544.0 |
| $C_{19}$ | 1288.3 |
| $A_{20}$ | 7831.1 |
| $B_{20}$ | 1541.4 |
| $C_{20}$ | 1287.4 |
| $A_{21}$ | 7876.4 |
| $B_{21}$ | 1546.4 |
| $C_{21}$ | 1287.4 |

Table 5: Full rotational constants for $c$-$C_3(CN)_2$.

| **Constant** | **F12-DZ Value (MHz)** | **F12-DZ-cCR Value (MHz)** | **F12-TZ Value (MHz)** |
|---|---|---|---|
| $A_e$ | 7907.6 | 7957.4 | 7913.6 |
| $B_e$ | 1558.9 | 1564.6 | 1560.7 |
| $C_e$ | 1302.3 | 1307.4 | 1303.8 |
| $A_0$ | 7917.1 | 7967.3 | 7923.0 |
| $B_0$ | 1558.0 | 1563.5 | 1559.8 |
| $C_0$ | 1300.2 | 1305.4 | 1301.6 |
| $A_1$ | 7895.9 | 7945.9 | 7901.6 |
| $B_1$ | 1554.9 | 1560.3 | 1556.6 |
| $C_1$ | 1297.5 | 1302.6 | 1298.9 |
| $A_2$ | 7898.5 | 7948.5 | 7904.1 |
| $B_2$ | 1554.9 | 1560.4 | 1556.7 |
| $C_2$ | 1297.5 | 1302.7 | 1298.9 |
| $A_3$ | 7860.7 | 7911.1 | 7866.5 |
| $B_3$ | 1556.5 | 1561.9 | 1558.3 |
| $C_3$ | 1297.7 | 1302.8 | 1299.1 |
| $A_4$ | 7896.2 | 7946.3 | 7902.1 |
| $B_4$ | 1557.7 | 1563.2 | 1559.5 |
| $C_4$ | 1299.3 | 1304.4 | 1300.7 |
| $A_5$ | 7941.8 | 7991.9 | 7948.5 |
| $B_5$ | 1551.2 | 1556.6 | 1552.9 |
| $C_5$ | 1295.8 | 1301.0 | 1297.2 |
| $A_6$ | 7886.8 | 7937.0 | 7892.4 |
| $B_6$ | 1559.8 | 1565.3 | 1561.6 |
| $C_6$ | 1300.4 | 1305.6 | 1301.8 |
| $A_7$ | 7970.6 | 8021.0 | 7977.4 |
| $B_7$ | 1551.6 | 1557.0 | 1553.3 |
| $C_7$ | 1297.1 | 1302.3 | 1298.5 |
| $A_8$ | 7941.7 | 7992.6 | 7948.2 |
| $B_8$ | 1557.2 | 1562.6 | 1558.9 |
| $C_8$ | 1300.8 | 1305.9 | 1302.1 |
| $A_9$ | 7885.4 | 7935.5 | 7891.6 |
| $B_9$ | 1561.7 | 1567.1 | 1563.4 |
| $C_9$ | 1301.5 | 1306.7 | 1302.9 |
| $A_{10}$ | 7908.2 | 7958.2 | 7913.1 |

| | | | |
|---|---|---|---|
| $B_{10}$ | 1560.5 | 1566.0 | 1562.4 |
| $C_{10}$ | 1302.2 | 1307.5 | 1303.7 |
| $A_{11}$ | 7946.4 | 7996.8 | 7952.5 |
| $B_{11}$ | 1558.3 | 1563.8 | 1560.1 |
| $C_{11}$ | 1300.4 | 1305.6 | 1301.8 |
| $A_{12}$ | 7937.8 | 7988.0 | 7943.5 |
| $B_{12}$ | 1560.0 | 1565.5 | 1561.8 |
| $C_{12}$ | 1301.7 | 1306.9 | 1303.0 |
| $A_{13}$ | 7915.2 | 7965.4 | 7920.4 |
| $B_{13}$ | 1560.9 | 1566.4 | 1562.7 |
| $C_{13}$ | 1303.0 | 1308.2 | 1304.4 |
| $A_{14}$ | 7923.9 | 7973.4 | 7928.5 |
| $B_{14}$ | 1558.9 | 1564.5 | 1560.8 |
| $C_{14}$ | 1302.2 | 1307.4 | 1303.6 |
| $A_{15}$ | 7966.5 | 8017.0 | 7972.3 |
| $B_{15}$ | 1563.7 | 1569.2 | 1565.5 |
| $C_{15}$ | 1302.1 | 1307.3 | 1303.5 |

Table 6: Full rotational constants for $c$-$C_3(C_2H)(CN)$.

| **Constant** | **F12-DZ Value (MHz)** |
|---|---|
| $A_e$ | 7863.9 |
| $B_e$ | 1551.1 |
| $C_e$ | 1295.7 |
| $A_0$ | 7866.6 |
| $B_0$ | 1550.6 |
| $C_0$ | 1293.6 |
| $A_1$ | 7861.2 |
| $B_1$ | 1549.6 |
| $C_1$ | 1292.8 |
| $A_2$ | 7844.4 |
| $B_2$ | 1547.7 |
| $C_2$ | 1291.0 |
| $A_3$ | 7847.0 |
| $B_3$ | 1547.7 |
| $C_3$ | 1291.1 |
| $A_4$ | 7813.0 |
| $B_4$ | 1549.0 |
| $C_4$ | 1291.1 |
| $A_5$ | 7856.1 |
| $B_5$ | 1548.9 |
| $C_5$ | 1292.0 |
| $A_6$ | 7880.2 |
| $B_6$ | 1545.5 |
| $C_6$ | 1290.2 |
| $A_7$ | 7834.0 |
| $B_7$ | 1552.7 |
| $C_7$ | 1293.9 |
| $A_8$ | 7926.1 |
| $B_8$ | 1550.5 |
| $C_8$ | 1293.7 |
| $A_9$ | 7926.5 |
| $B_9$ | 1543.9 |
| $C_9$ | 1290.5 |
| $A_{10}$ | 7887.6 |

| | |
|---|---|
| $B_{10}$ | 1550.3 |
| $C_{10}$ | 1294.3 |
| $A_{11}$ | 7798.9 |
| $B_{11}$ | 1551.9 |
| $C_{11}$ | 1294.2 |
| $A_{12}$ | 7838.9 |
| $B_{12}$ | 1553.9 |
| $C_{12}$ | 1294.8 |
| $A_{13}$ | 7847.2 |
| $B_{13}$ | 1553.4 |
| $C_{13}$ | 1295.7 |
| $A_{14}$ | 7893.4 |
| $B_{14}$ | 1551.1 |
| $C_{14}$ | 1293.9 |
| $A_{15}$ | 7890.0 |
| $B_{15}$ | 2023.8 |
| $C_{15}$ | 1295.1 |
| $A_{16}$ | 7863.5 |
| $B_{16}$ | 1296.3 |
| $C_{16}$ | 1082.3 |
| $A_{17}$ | 7869.1 |
| $B_{17}$ | 1551.4 |
| $C_{17}$ | 1295.5 |
| $A_{18}$ | 7926.8 |
| $B_{18}$ | 1555.5 |
| $C_{18}$ | 1295.1 |

# 3 Geometries

### 3.0.1 Reactants

| | | | |
|---|---|---|---|
| H | 0.0000000000 | 1.5722346313 | 2.0492555517 |
| C | 0.0000000000 | 0.6363761494 | 1.5151650591 |
| C | 0.0000000000 | -0.7768025200 | 1.5565393189 |
| C | 0.0000000000 | -0.0061721264 | 0.3481131700 |
| C | 0.0000000000 | 0.0083128029 | -1.0515125673 |
| C | 0.0000000000 | 0.0061338761 | -2.2612492530 |
| H | 0.0000000000 | 0.0025371677 | -3.3249727025 |
| T1 Diagnostic | | | 0.01384881 |
| D1 Diagnostic | | | 0.03488395 |

Table 7: Ethynyl cyclopropenylidene ($c$-$C_3HC_2H$). Cartesian coordinates in Å.

| | | | |
|---|---|---|---|
| C | 0.0000000000 | -0.0004487039 | -0.5378325822 |
| C | 0.0000000000 | 0.0002099726 | 0.6722838571 |
| H | 0.0000000000 | 0.0028448132 | -1.6021730094 |
| T1 Diagnostic | | | 0.01708698 |
| D1 Diagnostic | | | 0.03200616 |

Table 8: Ethynyl radical ($\cdot C_2H$). Cartesian coordinates in Å.

| | | | |
|---|---|---|---|
| C | 0.0000000000 | 0.7752365182 | -1.5721183315 |
| C | 0.0000000000 | -0.6443704939 | -1.5159518176 |
| C | 0.0000000000 | 0.0132035216 | -0.3625323573 |
| H | 0.0000000000 | -1.5885783366 | -2.0342174393 |
| C | 0.0000000000 | 0.0006151911 | 1.0468144092 |
| N | 0.0000000000 | -0.0097536698 | 2.2076768947 |
| T1 Diagnostic | 0.01428664 | | |
| D1 Diagnostic | 0.03441435 | | |

Table 9: Cyano cyclopropenylidene ($c$-$C_3HCN$). Cartesian coordinates in Å.

| | | | |
|---|---|---|---|
| C | 0.0000000000 | 0.0000000000 | -0.6318108729 |
| N | 0.0000000000 | 0.0000000000 | 0.5417893147 |
| T1 Diagnostic | 0.05258831 | | |
| D1 Diagnostic | 0.14909065 | | |

Table 10: Cyano radical (·CN). Cartesian coordinates in Å.

## 3.1 Products

| | | | |
|---|---|---|---|
| C | 0.0000000000 | 0.0000000000 | -1.7002361540 |
| C | 0.0000000000 | -0.6696911150 | -0.4412583928 |
| C | 0.0000000000 | 0.6696911150 | -0.4412583928 |
| C | 0.0000000000 | -1.8700825988 | 0.2778660817 |
| C | 0.0000000000 | 1.8700825988 | 0.2778660817 |
| C | 0.0000000000 | -2.9116059255 | 0.8933062038 |
| C | 0.0000000000 | 2.9116059255 | 0.8933062038 |
| H | 0.0000000000 | -3.8287692554 | 1.4323992076 |
| H | 0.0000000000 | 3.8287692554 | 1.4323992076 |
| T1 Diagnostic | | | 0.01477358 |
| D1 Diagnostic | | | 0.03541838 |

Table 11: Diethynyl cyclopropenylidene ($c$-$C_3(C_2H)_2$). Cartesian coordinates in Å.

| | | | |
|---|---|---|---|
| C | 0.0000000000 | 0.0000000000 | -1.7172663815 |
| C | 0.0000000000 | -0.6651752047 | -0.4515721350 |
| C | 0.0000000000 | 0.6651752047 | -0.4515721350 |
| C | 0.0000000000 | -1.8683390146 | 0.2801247855 |
| C | 0.0000000000 | 1.8683390146 | 0.2801247855 |
| N | 0.0000000000 | -2.8601895568 | 0.8833127981 |
| N | 0.0000000000 | 2.8601895568 | 0.8833127981 |
| T1 Diagnostic | | | 0.01538254 |
| D1 Diagnostic | | | 0.03457971 |

Table 12: Dicyano cyclopropenylidene ($c$-$C_3(CN)_2$). Cartesian coordinates in Å.

| | | | |
|---|---|---|---|
| C | 0.0000000000 | 1.7092000683 | 0.0031708212 |
| C | 0.0000000000 | 0.4473145319 | -0.6518590730 |
| C | 0.0000000000 | 0.4468864243 | 0.6835608224 |
| C | 0.0000000000 | -0.2886769435 | -1.8539013022 |
| N | 0.0000000000 | -0.8993134863 | -2.8413920376 |
| C | 0.0000000000 | -0.2685196897 | 1.8827538965 |
| C | 0.0000000000 | -0.8786251283 | 2.9270508219 |
| H | 0.0000000000 | -1.4161361986 | 3.8457799824 |
| T1 Diagnostic | | | |
| D1 Diagnostic | | | |

Table 13: Cyano ethynyl cyclopropenylidene ($c$-$C_3(C_2H)(CN)$). Cartesian coordinates in Å.

## 3.2 Intermediates

| | | | |
|---|---|---|---|
| H | 2.0594765220 | -1.5868212459 | 0.0000000000 |
| C | 1.7204690935 | -0.5718366082 | 0.0000000000 |
| C | 1.6162846894 | 0.6892539691 | 0.0000000000 |
| C | 0.1994992885 | 0.0954754765 | 0.0000000000 |
| C | -0.5416694407 | 0.0175063206 | 1.2123250231 |
| C | -0.5416694407 | 0.0175063206 | -1.2123250231 |
| C | -1.1684127422 | -0.0484255574 | 2.2374850946 |
| C | -1.1684127422 | -0.0484255574 | -2.2374850946 |
| H | -1.7214170524 | -0.1066002720 | 3.1420307624 |
| H | -1.7214170524 | -0.1066002720 | -3.1420307624 |
| T1 Diagnostic | | | 0.0177825 |
| D1 Diagnostic | | | 0.05873172 |

Table 14: $C_s$ isomer of $c$-$C_3(C_2H)_2$ I1. Cartesian coordinates in Å.

| | | | |
|---|---|---|---|
| C | 0.6532484934 | 0.1574171734 | 0.7466741569 |
| C | 1.5843289829 | 0.3862912094 | -0.1009239870 |
| C | -0.2088626531 | 0.0739956525 | 1.8046384576 |
| C | -1.0298519588 | -0.0689847782 | 2.6770752663 |
| H | -1.7525157753 | -0.1948412090 | 3.4450249942 |
| C | 0.6648597344 | -0.5498125823 | -0.8015342803 |
| H | 0.9059513723 | -1.6084737015 | -0.8072812906 |
| C | -0.3049094542 | -0.1270922253 | -1.7383368649 |
| C | -1.1316509454 | 0.2332826582 | -2.5369738755 |
| H | -1.8603875730 | 0.5509374270 | -3.2409376270 |
| T1 Diagnostic | | | 0.01696458 |
| D1 Diagnostic | | | 0.04763705 |

Table 15: $C_1$ isomer of $c$-$C_3(C_2H)_2$ I1. Cartesian coordinates in Å.

| | | | |
|---|---|---|---|
| H | -2.5019343323 | -0.7058512769 | 0.0000000000 |
| C | -1.7109502676 | 0.0401662271 | 0.0000000000 |
| C | -0.4216046498 | 0.0326084059 | 0.6670949512 |
| C | -0.4216046498 | 0.0326084059 | -0.6670949512 |
| C | 0.3091406562 | 0.0031839990 | 1.8400522340 |
| C | 0.9463892973 | -0.0224756436 | 2.8629331590 |
| H | 1.5077632147 | -0.0450800921 | 3.7640236202 |
| C | 0.3091406562 | 0.0031839990 | -1.8400522340 |
| C | 0.9463892973 | -0.0224756436 | -2.8629331590 |
| H | 1.5077632147 | -0.0450800921 | -3.7640236202 |
| T1 Diagnostic | | | 0.01593892 |
| D1 Diagnostic | | | 0.03677096 |

Table 16: $C_s$ isomer of *c*-$C_3(C_2H)_2$ I2. Cartesian coordinates in Å.

| | | | |
|---|---|---|---|
| H | 0.0000000000 | 0.0000000000 | -2.6099680133 |
| C | 0.0000000000 | 0.0000000000 | -1.5309933614 |
| C | 0.0000000000 | 0.7477826829 | -0.3988736444 |
| C | 0.0000000000 | -0.7477826829 | -0.3988736444 |
| C | 0.0000000000 | 1.9283117080 | 0.2765001821 |
| C | 0.0000000000 | 2.9821025376 | 0.8793678201 |
| H | 0.0000000000 | 3.9031625915 | 1.4063009491 |
| C | 0.0000000000 | -1.9283117080 | 0.2765001821 |
| C | 0.0000000000 | -2.9821025376 | 0.8793678201 |
| H | 0.0000000000 | -3.9031625915 | 1.4063009491 |
| T1 Diagnostic | | | 0.01635972 |
| D1 Diagnostic | | | 0.04247422 |

Table 17: $C_{2v}$ isomer of *c*-$C_3(C_2H)_2$ I2. Cartesian coordinates in Å.

| | | | |
|---|---|---|---|
| H | 2.1226792337 | -1.5620284674 | 0.0000000000 |
| C | 1.7384894977 | -0.5621493152 | 0.0000000000 |
| C | 1.6079163987 | 0.6959139558 | 0.0000000000 |
| C | 0.2295196009 | 0.0863303682 | 0.0000000000 |
| C | -0.5358181844 | 0.0117013949 | 1.2124612015 |
| C | -0.5358181844 | 0.0117013949 | -1.2124612015 |
| N | -1.1501120902 | -0.0481991149 | 2.1856361073 |
| N | -1.1501120902 | -0.0481991149 | -2.1856361073 |
| T1 Diagnostic | | | 0.02203788 |
| D1 Diagnostic | | | 0.08900599 |

Table 18: $C_s$ isomer of *c*-$C_3(CN)_2$ I1. Cartesian coordinates in Å.

| | | | |
|---|---|---|---|
| H | 0.0000000000 | 0.0000000000 | -2.6034009970 |
| C | 0.0000000000 | 0.0000000000 | -1.5251424952 |
| C | 0.0000000000 | 0.7402093914 | -0.3899768683 |
| C | 0.0000000000 | -0.7402093914 | -0.3899768683 |
| C | 0.0000000000 | 1.9350926650 | 0.2774024360 |
| C | 0.0000000000 | -1.9350926650 | 0.2774024360 |
| N | 0.0000000000 | 2.9497596545 | 0.8441253658 |
| N | 0.0000000000 | -2.9497596545 | 0.8441253658 |
| T1 Diagnostic | | | 0.01692309 |
| D1 Diagnostic | | | 0.04613679 |

Table 21: $C_{2v}$ isomer of *c*-$C_3(CN)_2$ I2. Cartesian coordinates in Å.

| | | | |
|---|---|---|---|
| C | 0.6556340243 | 0.5428565173 | -0.7926952793 |
| C | 1.5531518102 | -0.4064892366 | -0.0887102644 |
| C | 0.5995404959 | -0.1147024282 | 0.7121953596 |
| C | -0.2315290038 | -0.0386607265 | 1.8103668494 |
| N | -0.9472247025 | 0.0457887695 | 2.7135074862 |
| C | -0.2986086060 | 0.1039408546 | -1.7631533926 |
| N | -1.0724906790 | -0.2350348825 | -2.5475833614 |
| H | 0.9189264359 | 1.5937628915 | -0.8519820089 |
| T1 Diagnostic | | | 0.01981885 |
| D1 Diagnostic | | | 0.07082537 |

Table 19: $C_1$ isomer of $c$-$C_3(CN)_2$ I1. Cartesian coordinates in Å.

| | | | |
|---|---|---|---|
| C | -0.0006286648 | 1.5251196958 | 0.0000000000 |
| H | -0.0027654220 | 2.6033600865 | 0.0000000000 |
| C | 0.0008662339 | 0.3899652462 | -0.7402185300 |
| C | 0.0008662339 | 0.3899652462 | 0.7402185300 |
| C | 0.0001336751 | -0.2773995818 | -1.9351173380 |
| N | -0.0004883928 | -0.8441065997 | -2.9497910394 |
| C | 0.0001336751 | -0.2773995818 | 1.9351173380 |
| N | -0.0004883928 | -0.8441065997 | 2.9497910394 |
| T1 Diagnostic | | | 0.01613022 |
| D1 Diagnostic | | | 0.03392032 |

Table 20: $C_s$ isomer of $c$-$C_3(CN)_2$ I2. Cartesian coordinates in Å.

## 3.3 Transition States

| | | | |
|---|---|---|---|
| C | 0.0087607107 | -0.0248041735 | -0.0078770509 |
| C | 0.0114305673 | 0.0089205739 | 1.4281802018 |
| C | 1.3682544757 | 0.0005728098 | 1.0094216473 |
| H | 2.1588249660 | -0.6553675570 | 1.3616073691 |
| C | 1.3070283990 | 0.6648664042 | -0.3066765372 |
| C | 1.9270564515 | 1.3781556798 | -1.1666724573 |
| H | 2.4237788062 | 2.0461865856 | -1.8260460342 |
| C | -0.7197285211 | -0.8642763141 | -0.8726490775 |
| C | -1.3547799059 | -1.5383407855 | -1.6382960750 |
| H | -1.9226342103 | -2.1396617436 | -2.3044275161 |
| T1 Diagnostic | | | 0.01840354 |
| D1 Diagnostic | | | 0.05119619 |
| Imaginary Frequency | | | -529.4702 |

Table 22: $TS_{I1}$ (ethynyl migration). Cartesian coordinates in Å.

| | | | |
|---|---|---|---|
| H | -0.1630937500 | 0.0249259846 | 0.1189538980 |
| C | 0.1492970890 | 0.1308980678 | 1.1462651142 |
| C | 1.3348177667 | -0.0508981496 | 2.0199301467 |
| C | 0.5988730256 | 1.1056666001 | 1.9934944585 |
| C | 2.3758031939 | -0.7827814079 | 2.4897120657 |
| C | 3.3032161384 | -1.4561552383 | 2.8969153378 |
| H | 4.1140383706 | -2.0377341433 | 3.2567303559 |
| C | 0.4839986695 | 2.4177259728 | 2.4497275371 |
| C | 0.3842813799 | 3.5441304247 | 2.8563010492 |
| H | 0.2981099900 | 4.5401133867 | 3.2150415328 |
| T1 Diagnostic | | | 0.02351524 |
| D1 Diagnostic | | | 0.09558066 |
| Imaginary Frequency | | | -784.0172 |

Table 23: $TS_{I2}$ ($c$-$C_3H(C_2H)_2$ planarization). Cartesian coordinates in Å.

| | | | |
|---|---|---|---|
| C | 0.2168792222 | 0.7853122424 | 0.4219740829 |
| C | -0.2712027646 | -0.1267054775 | 1.3314244645 |
| C | 1.2439094698 | -0.2335425376 | 0.6064927050 |
| H | 2.2728256413 | -0.0209954722 | 0.8803817382 |
| C | -0.8566539994 | -0.0779836753 | 2.6078283872 |
| N | -1.3519481351 | -0.0796489665 | 3.6493871270 |
| C | 0.5872177333 | -1.4827235016 | 0.7825314814 |
| N | 0.3581085141 | -2.6610105613 | 0.6562608975 |
| T1 Diagnostic | | | 0.03013888 |
| D1 Diagnostic | | | 0.12776674 |
| Imaginary Frequency | | | -638.7282 |

Table 24: $TS_{I1}$ (cyano migration). Cartesian coordinates in Å.

| | | | |
|---|---|---|---|
| H | -0.0920212447 | 0.0970311001 | 0.2045210402 |
| C | 0.0684798790 | 0.0940540003 | 1.2724732279 |
| C | 1.1706754165 | -0.2124716671 | 2.2252994317 |
| C | 0.5415046236 | 0.9807317854 | 2.2188101471 |
| C | 2.1192009092 | -1.0534703024 | 2.7423976799 |
| N | 2.9201761376 | -1.7824284139 | 3.1635097538 |
| C | 0.4940272811 | 2.2762267861 | 2.7548613891 |
| N | 0.4465528918 | 3.3405508375 | 3.1929359252 |
| T1 Diagnostic | | | 0.03143302 |
| D1 Diagnostic | | | 0.15095266 |
| Imaginary Frequency | | | -674.8520 |

Table 25: $TS_{I2}$ ($c$-$C_3H(CN)_2$ planarization). Cartesian coordinates in Å.

### 3.4 QFF Product Geometries

| | | | |
|---|---|---|---|
| C | 0.0000000000 | 0.0000000000 | -1.7002127507 |
| C | 0.0000000000 | -0.6697694910 | -0.4403879631 |
| C | 0.0000000000 | 0.6697694910 | -0.4403879631 |
| C | 0.0000000000 | -1.8711542164 | 0.2786442150 |
| C | 0.0000000000 | -2.9146781494 | 0.8918147824 |
| H | 0.0000000000 | -3.8324084547 | 1.4303872059 |
| C | 0.0000000000 | 1.8711542164 | 0.2786442150 |
| C | 0.0000000000 | 2.9146781494 | 0.8918147824 |
| H | 0.0000000000 | 3.8324084547 | 1.4303872059 |

Table 26: Optimized Cartesian Geometry for $C_7H_2$ at the F12-DZ level of theory in Å.

| | | | |
|---|---|---|---|
| C | 0.0000000000 | 0.0000000000 | -1.7171756332 |
| C | 0.0000000000 | -0.6652632906 | -0.4505180006 |
| C | 0.0000000000 | 0.6652632906 | -0.4505180006 |
| C | 0.0000000000 | -1.8695189799 | 0.2811143612 |
| N | 0.0000000000 | -2.8636031948 | 0.8815213703 |
| C | 0.0000000000 | 1.8695189799 | 0.2811143612 |
| N | 0.0000000000 | 2.8636031948 | 0.8815213703 |

Table 27: Optimized Cartesian Geometry for $C_5N_2$ at the F12-DZ level of theory in Å.

| | | | |
|---|---|---|---|
| C | 0.0000000000 | 0.0000000000 | -1.7124100816 |
| C | 0.0000000000 | -0.6640631126 | -0.4491069481 |
| C | 0.0000000000 | 0.6640631126 | -0.4491069481 |
| C | 0.0000000000 | -1.8666824539 | 0.2802048376 |
| N | 0.0000000000 | -2.8594083346 | 0.8790480267 |
| C | 0.0000000000 | 1.8666824539 | 0.2802048376 |
| N | 0.0000000000 | 2.8594083346 | 0.8790480267 |

Table 28: Optimized Cartesian Geometry for $C_5N_2$ at the F12-DZ-cCR level of theory in Å.

| | | | |
|---|---|---|---|
| C | 0.0000000000 | 1.7093717311 | 0.0037429947 |
| C | 0.0000000000 | 0.4467218930 | -0.6519716194 |
| C | 0.0000000000 | 0.4455792175 | 0.6834530623 |
| C | 0.0000000000 | -0.2888089283 | -1.8553403844 |
| N | 0.0000000000 | -0.8978937546 | -2.8443143200 |
| C | 0.0000000000 | -0.2701428232 | 1.8833226149 |
| C | 0.0000000000 | -0.8776554970 | 2.9297990611 |
| H | 0.0000000000 | -1.4141171242 | 3.8493321739 |

Table 29: Optimized Cartesian Geometry for $C_6NH$ at the F12-DZ level of theory in Å.