**Supporting Information for**

**Bottom-up Formation of Antiaromatic Cyclobutadiene (*c*-C4H4) in Interstellar Ice Analogs**

Jia Wang,1,2 Joshua H. Marks,1,2 André K. Eckhardt,3\* Ralf I. Kaiser1,2\*

*1 W. M. Keck Research Laboratory in Astrochemistry, University of Hawaii at Manoa, Honolulu, HI 96822, USA*

*2 Department of Chemistry, University of Hawaii at Manoa, Honolulu, HI 96822, USA*

*3 Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, Bochum 44801, Germany*

\*Corresponding Authors: [Andre.Eckhardt@ruhr-uni-bochum.de](mailto:Andre.Eckhardt@ruhr-uni-bochum.de), [ralfk@hawaii.edu](mailto:ralfk@hawaii.edu)

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**Figure S1.** Infrared spectra of an acetylene (C2H2) ice before (black) and after (red) electron irradiation at 5 K with magnified view and deconvolution of the region 3400–2800 cm−1 (**b**) and region 1700–900 cm−1 (**c**). Detailed assignments are compiled in Table S1.

A graph of a red line and black line

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**Figure S2**. Simulated ultraviolet (UV) spectra of isomers **1**, **2**, and **8** calculated at the TD-B3LYP/cc-pVTZ level of theory. The spectra were convoluted using a Gaussian line shape function with a full width at half maximum (FWHM) of 20 nm.

**Table S1.** Infrared absorption features observed in acetylene (C2H2) ices before and after electron irradiation at 5 K. Assignment labels: stretching (ν) and bending (δ).

|  |  |  |
| --- | --- | --- |
| Absorption position (cm−1) |  |  |
| Before irradiation | Assignment | References |
| 4067 | ν1 + ν5 | Ref.[1-3](#_ENREF_1) |
| 3861 | ν3 + 2ν4 + ν5 | Ref.[1](#_ENREF_1),[2](#_ENREF_2) |
| 3330 | ν1 | Ref.[1](#_ENREF_1),[2](#_ENREF_2) |
| 3235 | ν3 | Ref.[1](#_ENREF_1),[2](#_ENREF_2) |
| 3006 | ν3 (13C2H2) | Ref.[1-3](#_ENREF_1) |
| 2707 | ν2 + ν5 | Ref.[1](#_ENREF_1),[3](#_ENREF_3) |
| 2549 | ν3 (C2DH) | Ref.[1](#_ENREF_1) |
| 1959 | ν2 | Ref.[1](#_ENREF_1) |
| 1410 | ν4 + ν5 | Ref.[2](#_ENREF_2) |
| 1393 | ν6 | Ref.[1](#_ENREF_1),[2](#_ENREF_2) |
| 774, 748 | ν5 | Ref.[3](#_ENREF_3),[4](#_ENREF_4) |
| After irradiation | Assignment | References |
| 3325 | ν4 (C4H2) | Ref.[1](#_ENREF_1) |
| 3284 | ν1 (**7**) | Ref.[1](#_ENREF_1) |
| 3157a | νCH (R-CHCH2) /ν1 (**1**) | Ref.[1](#_ENREF_1),[5](#_ENREF_5) |
| 3090a | ν9 (C2H4) /ν15 (**1**) | Ref.[1](#_ENREF_1),[5](#_ENREF_5) |
| 3049 | ν(CH) | Ref.[6](#_ENREF_6),[7](#_ENREF_7) |
| 3033 | ν18 (C6H6)/νCH (aromatic) | Ref.[1](#_ENREF_1) |
| 2974 | ν6+ν7 (**7**) /ν11 (C2H4) | Ref.[1](#_ENREF_1),[7](#_ENREF_7) |
| 2926 | νCH (alkyl) | Ref.[4](#_ENREF_4),[6](#_ENREF_6) |
| 2880 | ν5 (C2H6) | Ref.[1](#_ENREF_1) |
| 1599 | ν6 (**7**) | Ref.[1](#_ENREF_1),[7](#_ENREF_7) |
| 1435 | ν12 (C2H4) | Ref.[8](#_ENREF_8),[9](#_ENREF_9) |
| 1005a | ν10 (*c*-C3H6) / ν10 (**1**) | Ref.[5](#_ENREF_5),[9](#_ENREF_9),[10](#_ENREF_10) |
| 978 | ν14 (**7**) | Ref.[7](#_ENREF_7) |
| 959 | δCH (substituted benzenes) | Ref.[3](#_ENREF_3),[4](#_ENREF_4) |

a The absorption band is tentatively assigned to cyclobutadiene (**1**) based on the scaled frequencies calculated at the CCSD(T)=FULL/aug-cc-pVTZ level of theory.[5](#_ENREF_5)

**Table S2.** Error analysis of adiabatic ionization energies (IEs) and relative energies (∆E) of distinct C4H4 isomers. IEs and ∆E were computed at the CCSD(T)/CBS//B3LYP/cc-pVTZ level of theory including the zero-point vibrational energy corrections. The computed Cartesian coordinates and vibrational frequencies of neutral and ionic species are listed in Table S5. The IE ranges were corrected for thermal and Stark effects by −0.03 eV.[11](#_ENREF_11)

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Isomer | Structure | ∆E  (kJ mol−1) | Experimental IE (eV) | Computed  IE (eV) | IE difference to lower bound (eV) | IE difference to upper bound (eV) | IE range after error analysis (eV) |
| Cyclobutadiene  **1** | A grey and white molecule structure  Description automatically generated | 141 |  | 8.00 |  |  | 7.94 – 8.04 |
| Tetrahedrane  **2** | A grey and white molecule structure  Description automatically generated | 249 |  | 8.06 |  |  | 8.00 – 8.10 |
| Vinylacetylene  **7** | A grey and white molecule model  Description automatically generated | 0 | 9.58 ± 0.02[9](#_ENREF_9) | 9.59 | −0.03 | 0.01 | 9.53 – 9.63 |
| Methylenecyclopropene  **8** | A grey and white molecule model  Description automatically generated | 98 | 8.15 ± 0.03[9](#_ENREF_9),[12](#_ENREF_12) | 8.11 | 0.01 | 0.07 | 8.05 – 8.15 |
| 1,2,3-Butatriene  **9** | A grey spheres on a white background  Description automatically generated | 32 | 9.15 ± 0.02[9](#_ENREF_9),[13](#_ENREF_13) | 9.14 | −0.01 | 0.03 | 9.08 – 9.18 |
| Bicyclo[1.1.0]but-3(1)-ene  **10** | A grey molecule structure with balls  Description automatically generated | 280 |  | 9.12 |  |  | 9.06 – 9.16 |
|  |  |  |  |  | Average  −0.01 ± 0.02 | Average  +0.04 ± 0.03 |  |
|  |  |  |  |  | Combined error limits  −0.03 – +0.07 | |  |

**Table S3.** Experimental conditions of acetylene (C2H2) ices including ice thickness, irradiation parameters, and vacuum ultraviolet (VUV) photon energy.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Exp. | Thickness (nm) | Current  (nA) | Irradiation  time (s) | Dose (eV/ acetylene) | Photon energy (eV) | Notes |
| 1 | 830 ± 50 | - | - | - | 8.20 | Blank |
| 2 | 830 ± 50 | 109 ± 2 | 3600 ± 10 | 9.4 ± 1.5 | 8.20 |  |
| 3 | 830 ± 50 | 106 ± 2 | 3600 ± 10 | 9.1 ± 1.4 | 8.20 | Repeat Exp. 2 |
| 4 | 830 ± 50 | 107 ± 2 | 3600 ± 10 | 9.2 ± 1.4 | 8.20 | Repeat Exp. 2 |
| 5 | 830 ± 50 | 106 ± 2 | 3600 ± 10 | 9.1 ± 1.4 | 7.80 |  |
| 6 | 830 ± 50 | 107 ± 2 | 3600 ± 10 | 9.2 ± 1.4 | 8.20 | 299 nm photolysis after irradiation |
| 7 | 830 ± 50 | 106 ± 2 | 3600 ± 10 | 9.1 ± 1.4 | 8.20 | Repeat Exp. 6 |
| 8 | 850 ± 50 | 107 ± 2 | 3600 ± 10 | 9.2 ± 1.4 | 8.20 | Repeat Exp. 6 |
| 9 | 850 ± 50 | 111 ± 4 | 3600 ± 10 | 9.5 ± 1.5 | 8.20 | 221 nm photolysis after irradiation |

**Table S4.** Parameters for the generation of VUV light. The uncertainty for VUV photon energies is less than 0.001 eV.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| VUV photon energy (eV) | Nonlinear medium in four-wave mixing | ω1 laser  wavelength (nm) | ω1 Dye | ω2 laser wavelength (nm) | ω2 Dye |
| 8.20  (2ω1 − ω2) | Xenon | 249.628 | Coumarin 503 | 715.207 | LDS 722 |
| 7.80  (2ω1 − ω2) | Xenon | 249.628 | Coumarin 503 | 581.119 | Pyrromethene 597 |

**Table S5.** Cartesian coordinates for selected structures of C4H4 isomers. B3LYP/cc-pVTZ optimized Cartesian geometry (distances in Å), electronic energies (in hartree), frequencies (cm−1) intensities (km mol−1), zero-point vibrational energies (ZPVE), extrapolated CCSD(T)/CBS energies (in hartree) and adiabatic ionization energies (IEs) at CCSD(T)/CBS//B3LYP/cc-pVTZ level of theory.

|  |
| --- |
| **1** radical cation (D2h)  C –0.000000 0.686599 0.750341  C –0.000000 –0.686599 0.750341  C 0.000000 0.686599 –0.750341  C 0.000000 –0.686599 –0.750341  H –0.000000 1.453721 1.511268  H –0.000000 –1.453721 1.511268  H 0.000000 –1.453721 –1.511268  H 0.000000 1.453721 –1.511268  E = –154.4542317  ZPVE = 38.8741 kcal mol–1  **Frequency Intensity**  276.0704 0.0000  640.4900 84.1796  832.2695 0.9987  841.6395 0.0000  880.8589 0.0000  971.9317 0.0000  991.5550 0.0000  1027.8602 0.0000  1059.1926 1.1356  1211.1668 0.0000  1232.5650 0.0000  1305.0201 71.9589  1491.3494 89.5850  1511.5238 0.0000  3204.7286 0.0000  3226.8412 49.5164  3239.8058 28.6363  3247.9658 0.0000  **1** (D2h)  C 0.664400 –0.000000 –0.787600  C –0.664400 –0.000000 –0.787600  C 0.664400 0.000000 0.787600  C –0.664400 0.000000 0.787600  H 1.427549 –0.000000 –1.550163  H –1.427549 –0.000000 –1.550163  H –1.427549 0.000000 1.550163  H 1.427549 0.000000 1.550163  E = –154.7349854  ZPVE = 38.2835 kcal mol–1  **Frequency Intensity**  540.8596 0.0000  587.3077 127.2477  604.2518 0.0000  698.4518 9.4786  852.3092 0.0000  889.3490 0.0000  890.7646 0.0000  952.1803 0.0000  1060.4766 0.0901  1111.8341 0.0000  1192.7936 0.0000  1265.2261 39.0248  1626.9288 0.0000  1633.6769 4.5552  3193.5687 0.0000  3209.0823 12.8147  3230.1635 20.7511  3240.4735 0.0000 |
| **2** radical cation (C1)  C –0.592346 –0.607635 0.382981  C –0.607678 0.592308 –0.382984  C 0.607676 –0.592305 –0.382987  C 0.592342 0.607630 0.382992  H –1.174862 1.144947 –1.113087  H 1.145233 1.174579 1.113087  H 1.174901 –1.144918 –1.113078  H –1.145244 –1.174591 1.113066  E = –154.4046128  ZPVE = 36.9385 kcal mol–1  **Frequency Intensity**  485.9159 0.0000  612.6863 13.2732  648.9106 48.8967  709.1626 0.0000  759.4133 0.0000  764.8516 46.0211  764.8893 46.0190  930.4649 0.0000  999.4507 24.9013  999.4625 24.8847  1045.2343 0.0000  1306.5094 3.0925  1306.6953 3.0815  1445.3571 0.0000  3255.0240 100.4067  3258.3457 112.9764  3258.3500 112.9214  3288.0964 0.0000  **2** (Td)  C 0.521179 0.521179 0.521179  C –0.521179 –0.521179 0.521179  C 0.521179 –0.521179 –0.521179  C –0.521179 0.521179 –0.521179  H –1.137600 –1.137600 1.137600  H –1.137600 1.137600 –1.137600  H 1.137600 –1.137600 –1.137600  H 1.137600 1.137600 1.137600  E = –154.6957648  ZPVE = 37.3359 kcal mol–1  Frequency Intensity  574.7036 0.0000  574.7036 0.0000  774.7601 65.6948  774.7601 65.6948  774.7601 65.6948  843.6015 0.0000  843.6016 0.0000  891.6832 0.0000  891.6832 0.0000  891.6833 0.0000  1149.5326 2.9279  1149.5326 2.9279  1149.5326 2.9279  1458.2091 0.0000  3334.1033 11.8500  3334.1033 11.8500  3334.1033 11.8500  3371.7694 0.0000 |
| **7** radical cation (Cs)  C 0.621817 –0.528679 0.000000  C –0.138053 –1.687735 0.000000  H 0.343051 –2.657611 0.000000  H –1.219991 –1.648712 0.000000  C 0.036481 0.714859 –0.000000  H 1.706165 –0.584653 0.000000  C –0.463499 1.832286 –0.000000  H –0.902586 2.808515 –0.000000  E = –154.4588263  ZPVE = 37.6867 kcal mol–1  **Frequency Intensity**  211.0198 5.5624  278.5302 13.1006  519.5787 1.7658  551.5130 9.3273  680.0409 48.3325  773.3045 13.8438  891.7525 27.4534  937.1157 0.9330  1066.2661 9.1755  1133.1350 0.5054  1278.6399 30.4247  1437.5286 65.2393  1538.2685 38.7268  2123.8653 122.3631  3146.2361 16.1624  3156.3567 15.0496  3256.4676 15.3200  3382.5859 138.8371  **7** (Cs)  C –0.674648 –0.467653 0.000000  C –1.690583 0.396652 0.000000  H –2.713562 0.048104 0.000000  H –1.525819 1.465184 0.000000  C 0.697193 –0.099614 –0.000000  H –0.878465 –1.533400 0.000000  C 1.867876 0.174579 –0.000000  H 2.898441 0.426808 –0.000000  E = –154.7979450  ZPVE = 38.2649 kcal mol–1  **Frequency Intensity**  225.9582 2.6766  320.5892 8.8670  559.7306 4.9591  649.3593 47.2681  675.8635 44.5507  706.9073 1.7781  893.0959 2.2555  962.5901 42.3668  1012.8555 14.7567  1114.7889 3.7489  1325.6964 0.4594  1449.4179 3.0436  1669.2591 9.4554  2204.9388 0.4066  3137.4281 4.9392  3149.7069 3.3775  3237.4324 6.1240  3471.0886 70.8762 |
| **8** radical cation (C2v)  C 0.000000 0.674371 –1.010628  C –0.000000 –0.674371 –1.010628  C –0.000000 –0.000000 0.194911  H 0.000000 1.600278 –1.564602  H –0.000000 –1.600278 –1.564602  C –0.000000 –0.000000 1.597774  H –0.000000 0.935016 2.139718  H –0.000000 –0.935016 2.139718  E = –154.4690262  ZPVE = 37.8093 kcal mol–1  **Frequency Intensity**  235.7671 0.0000  360.2077 4.5638  419.2655 20.0369  817.4191 5.9055  837.0901 0.1387  880.0582 58.6573  953.4758 2.1478  991.1747 0.0000  1000.8620 28.5731  1082.0881 8.4150  1268.8218 24.6507  1441.1377 47.5163  1477.9502 31.1013  1743.9048 18.6326  3154.9643 18.1242  3239.0267 75.6043  3270.9076 10.4368  3273.8833 39.0069  **8** (C2v)  C 0.000000 0.656758 –1.002837  C –0.000000 –0.656758 –1.002837  C –0.000000 –0.000000 0.275660  H 0.000000 1.567085 –1.576184  H –0.000000 –1.567085 –1.576184  C –0.000000 –0.000000 1.600737  H –0.000000 0.926314 2.156709  H –0.000000 –0.926314 2.156709  E = –154.7616607  ZPVE = 37.9782 kcal mol–1  Frequency Intensity  360.8519 3.3816  430.8942 24.5831  686.6364 35.2667  715.9854 0.0000  775.6980 70.6166  841.9014 0.4481  849.6912 6.1322  913.8828 0.0000  1023.4632 8.0831  1069.2797 8.2380  1124.7067 10.5199  1460.7691 1.6649  1603.8735 25.3360  1824.9957 206.1271  3144.8718 3.6077  3226.2421 11.5584  3235.5897 0.7843  3276.7831 1.8580 |
| **9** radical cation (D2)  C 0.000000 0.000000 –0.629535  C 0.000000 –0.000000 –1.953708  H 0.318309 0.876968 –2.512401  H –0.318309 –0.876968 –2.512401  C –0.000000 0.000000 0.629535  C –0.000000 0.000000 1.953708  H 0.318309 –0.876968 2.512401  H –0.318309 0.876968 2.512401  E = –154.4657874  ZPVE = 36.5689 kcal mol–1  **Frequency Intensity**  205.4230 14.1285  211.8713 14.4922  370.9531 0.2673  497.7136 0.3058  695.7925 0.0000  881.3679 0.0000  953.8952 0.9512  954.8397 31.9212  991.5916 26.4948  1000.8181 3.6934  1370.3175 70.7033  1425.3344 0.0000  1561.4705 2.2031  1897.1491 0.0000  3093.9898 0.0000  3095.7078 164.0098  3186.0397 75.6746  3186.0506 9.4056  **9** (D2)  C 0.000000 0.631692 –0.000000  C 0.000000 1.943248 –0.000000  H –0.924750 2.507776 0.000231  H 0.924750 2.507776 –0.000231  C –0.000000 –0.631692 –0.000000  C –0.000000 –1.943248 –0.000000  H 0.924750 –2.507776 0.000231  H –0.924750 –2.507776 –0.000231  E = –154.7925173  ZPVE = 37.6236 kcal mol–1  **Frequency Intensity**  225.1199 6.9536  230.6334 6.0168  362.2186 0.0000  574.8887 0.0000  778.2503 0.0000  891.4062 0.0000  895.3525 95.1505  904.5415 0.0000  1026.1528 0.0000  1045.5381 0.7686  1412.5879 0.0359  1471.2333 0.0000  1681.6450 21.5846  2199.1118 0.0000  3116.5403 0.0000  3119.4130 6.1441  3191.5661 4.6841  3191.8699 0.0000 |
| **10** radical cation (C2)  C 0.676053 0.375244 0.151142  C –0.596733 1.075098 0.151266  C –0.676053 –0.375244 0.151142  H –0.898590 1.618931 –0.755586  H –0.898591 1.618932 1.058096  C 0.596733 –1.075098 0.151266  H 0.898591 –1.618932 1.058096  H 0.898590 –1.618931 –0.755586  E = –154.3540120  ZPVE = 36.4443 kcal mol–1  **Frequency Intensity**  251.2275 17.0642  545.3570 98.0578  840.3421 0.0000  847.8097 0.0000  868.2537 0.0000  886.2857 0.0000  944.6038 0.0000  954.9375 3.9879  1074.9159 44.0676  1120.4299 0.0000  1143.4530 0.0000  1328.7677 37.8635  1398.2172 0.0000  1417.9691 55.3693  2931.9543 137.4841  2963.0963 0.0008  2983.2028 0.0003  2992.3519 103.2850  **10** (C2)  C 0.000006 0.681976 –0.376604  C –1.228680 0.000001 0.115464  C –0.000006 –0.681976 –0.376604  H –2.054448 0.000006 –0.581041  H –1.524452 –0.000011 1.166788  C 1.228680 –0.000001 0.115464  H 1.524452 0.000011 1.166788  H 2.054448 –0.000007 –0.581041  E = –154.6831688  ZPVE = 38.8382 kcal mol–1  **Frequency Intensity**  367.2913 3.7531  406.2638 138.5603  717.1912 0.0000  931.6230 15.3382  934.6460 1.7423  1068.0418 0.9411  1072.3402 15.0439  1108.2552 0.0000  1134.7274 1.3147  1163.3747 0.0000  1336.9641 31.2257  1411.2847 1.7210  1515.2500 5.0124  1557.6431 2.0370  3031.3870 69.2944  3032.3357 67.3020  3188.3766 3.8315  3190.7425 3.8634 |

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