IDENTIFYING AN UNKNOWN ISOMER OF C_7H_7 OBSERVED IN JET-COOLED HYDROCARBON DISCHARGES

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We describe on-going efforts to diagnose the hydrocarbon carrier of an electronic band system observed near 459 nm. The spectral carrier can be produced in jet-cooled discharges of toluene and linear and cyclic heptatrienes, but is most efficiently generated from 1,6-heptadiyne. The spectrum is observed at $m/z = 91$ by resonant two-colour ionization, has an origin at the same wavelength in Ne and Ar expansions, and almost certainly does not result from photofragmentation of heavier species. Several ground-state frequencies have been obtained from single-vibronic-level emission (SVLE) spectroscopy. Optical-optical hole-burning and two-colour ion-yield measurements reveal that the spectrum arises from a single isomer with an adiabatic ionization energy near 6.93 eV. On this basis, a large number of C_7H_7 radicals can be simply ruled out using relatively inexpensive electronic structure calculations. The resonance-stabilized, substituted allylic radicals 1,2,5,6-heptatetraen-4-yl and 2-ethynylcyclopentenyl have predicted (CBS-QB3) AIEs within ~ 0.1 eV of experiment, but simulations of Franck-Condon activity in totally symmetric modes from CCSD and EOM-CCSD calculations disagree qualitatively with the experimental origin SVLE spectrum, for both isomers. The 1-ethynylcyclopentenyl radical, which can be viewed as hosting an embedded, strained 1-vinylpropargyl radical chromophore (absorbing near 462 nm), is under investigation at the time of writing.