

Significant progress has been made on radicals representing known or potentially important minima on four potential energy surfaces of high significance to petroleum combustion and pyrolysis (see, e.g., ref. 1): C_5H_5 , C_7H_5 , C_7H_7 , and C_9H_9 .

1. Spectroscopic identification of 1-ethynylcyclopent-2-en-1-yl, a new resonance-stabilized C_7H_7 radical

Myriad stable isomers of benzyl radical have been proposed as important intermediates in its decomposition², but only three - benzyl, troyl, and vinylcyclopentadienyl - have been detected with certainty, and only the former two have been studied in spectroscopic detail. Under the auspices of this grant, we observed the electronic spectrum of a previously unreported C_7H_7 radical near 459 nm using mass-selected resonant two-colour two-photon ionization (Fig. 1). After conducting a battery of spectroscopic and chemical tests, we have recently identified the spectral carrier with high confidence. The radical was first detected in co-existence with benzyl. It can be generated in jet-cooled discharges of a variety of C_7H_8 precursors - including, importantly, toluene - but is most efficiently produced from 1,6-heptadiyne. Optical-optical holeburning and two-colour ion-yield measurements reveal that the spectrum arises from a single isomer with an adiabatic ionization energy (AIE) near 6.93 eV. CBS-QB3 and B3LYP/TD-B3LYP calculations were used to coarsely constrain the range of isomers for consideration; AIEs of the most promising candidates were computed using high-level coupled cluster methods. The CCSD(T)/pVQZ AIE of 1-ethynylcyclopent-2-en-1-yl radical (Fig. 1), including zero-point energy, is within 0.01 eV of experiment. Moreover, a simulated *a*-type rotational envelope of the origin band using minimally adjusted B3LYP/TD-B3LYP rotational constants is consistent with observation, and a convincing assignment of several low-frequency features in single vibronic level emission spectra can be made using predicted ground state frequencies of 1-ethynylcyclopentenyl radical. This species can be viewed as harboring a *trans*-1-vinylpropargyl radical chromophore, on which basis its putative detection at a nearby wavelength (*trans*-1-vinylpropargyl absorbs near 462 nm) is unsurprising. In the 1,6-heptadiyne discharge, it is readily conceivable that 1-ethynylcyclopentenyl is formed by intramolecular reaction of a substituted propargyl radical derived directly from the precursor by cleavage of the weakest C-H bond. Its formation route in the toluene discharge is less obvious, though at high concentrations of toluene (and thus also, in the discharge, atomic hydrogen) it is possible that it could result from H-atom addition to ethynylcyclopentadiene (C_7H_6), a significant intermediate in the Benson fragmentation scheme³, which has been established as the primary thermal decomposition pathway for benzyl radical. Searches for other putatively stable C_7H_7 radicals are on-going.

2. Ionization energies and electronic spectroscopy of *cis* and *trans* 1-vinylpropargyl radicals (C_5H_5)

The resonance-stabilized 1-vinylpropargyl radical (1vpr), which can adopt *cis*- and *trans*- conformations, is held to be a significant intermediate in hydrocarbon pyrolysis combustion, having been putatively detected in flames of various fuels⁴, as well as in the formation and decomposition of benzyl radical^{5,6}. It has also been observed in the crossed-beam reaction of C_2 with propyne⁷, rendering it a species of potential importance in dense interstellar clouds. We have cleanly generated 1vpr in a discharge of pent-1-ene-4-yne and measured the adiabatic ionization energy (AIE) of each conformer by two-colour ion-yield spectroscopy. Our work takes advantage of an earlier report by one of us of the 1vpr electronic origin bands near 460 nm and 470 nm. Extrapolation to zero-field yields AIEs of 7.823(1) eV and 7.894(1) eV for the *trans*- and *cis*- forms respectively, in superb agreement with a QCISD(T) calculation (Hansen *et al.*, J. Phys. Chem. A 2006, 110, 4376-4388), and further supporting the identification of 1vpr in flames. In addition, we have secured vibrational assignments for a number of levels in the ground and first excited states of both conformers, first by decomposing the mass-resolved electronic spectrum (as much as possible) into *cis*- and *trans*-contributions using hole-

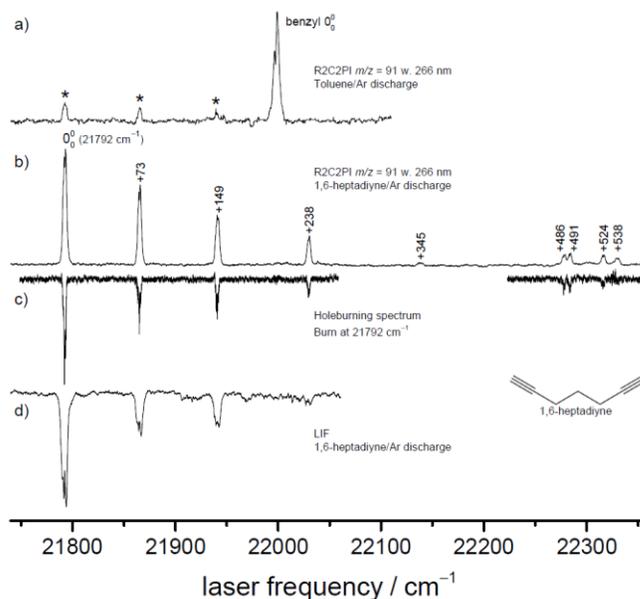


Fig. 1: (a) Electronic spectrum of a new C_7H_7 isomer first observed in toluene discharge; (b) after optimization with 1,6-heptadiyne; (c) holeburning spectrum (d) fluorescence detection.

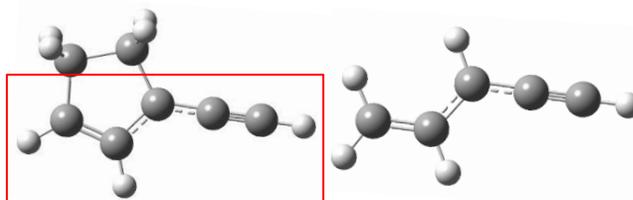


Fig. 2: Left: The 1-ethynylcyclopent-2-en-1-yl radical, with the red box highlighting the embedded *trans*-1-vinylpropargyl chromophore (shown at right). The newly detected radical may be formed by H-addition to ethynylcyclopentadiene under combustion conditions.

burning spectroscopy, and then by measuring SVLE spectra for sufficiently well-resolved bands. B3LYP and CASSCF calculations imply a non-planar D_1 geometry due to an out-of-plane dislocation of the acetylenic hydrogen atom, yielding Duschinsky matrices that are not block-diagonal. Nevertheless, these matrices provide valuable guidance for the assignment of multiple false origins that are conspicuous in SVLE spectra from low-frequency, nominally a'' modes.

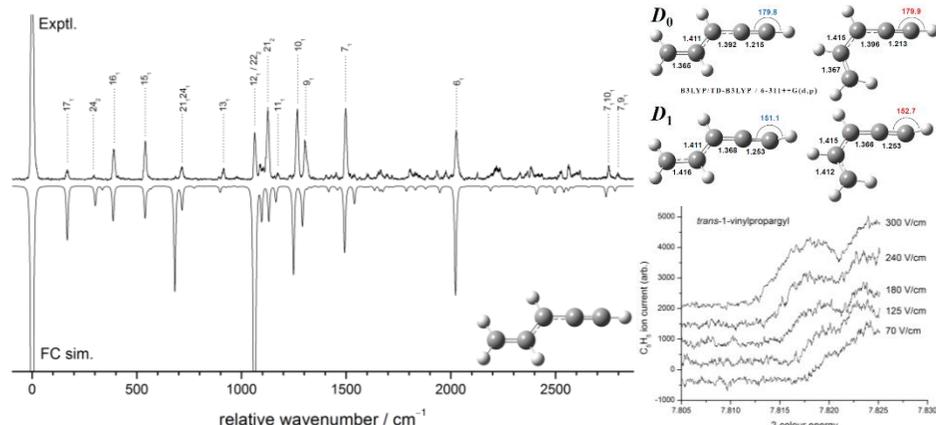


Fig. 3: Origin SVLE spectrum of *trans*-1-vinylpropargyl radical, with reflected Franck-Condon simulation, including Duschinsky rotation, using the optimized structures shown above right. Lower right: Field-correcting AIE measurements of the *trans*-1-vinylpropargyl AIE.

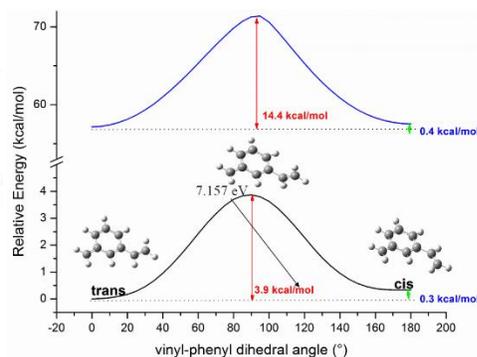
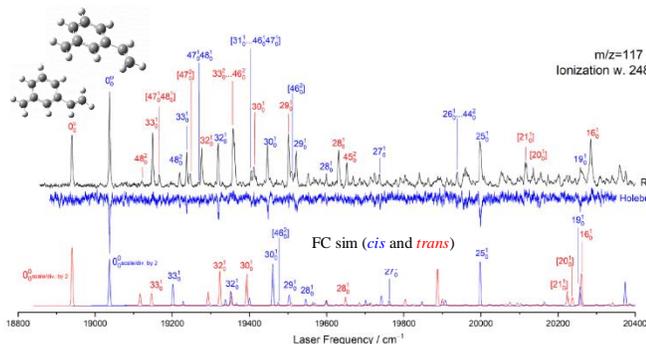
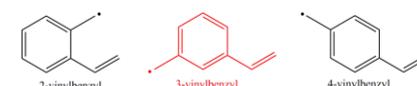


Fig. 4: Far left: Mass-selected electronic spectra of *cis* and *trans*-*m*-vinylbenzyl radicals, with *cis*-only spectrum reflected. Conformational identifications are supported by relaxed vinyl rotation scans (near left) and ground state vibrational frequencies obtained from single vibronic level fluorescence spectra.

3. Electronic spectra of vinylbenzyl (C_9H_9) and ethynylbenzyl (C_9H_7) radicals

Of the many possible isomers of C_9H_9 , only the global minimum, 1-indanyl, and the next most stable form, 1-phenylallyl, have been studied spectroscopically. Because of their extensive conjugation, the *o*-, *m*-, and *p*-vinylbenzyl radicals (below) should be endowed with significant resonance stabilization.



The group of Maier recently reported the detection in a heptadiyne discharge of one or more C_9H_9 radicals that exhibited absorption bands in near coincidence with some diffuse interstellar bands⁸. They posited that vinylbenzyl radicals (particularly *para*) were plausible carriers, a conjecture that is “readily” tested by interrogating jet-cooled toluene discharges in the optical band. Thus far, we have observed and carried out a detailed study of the *m*-vinylbenzyl radical (*cis* and *trans*, Fig. 4). The AIE is near 7.16 eV, rendering the neutral species of little relevance to diffuse interstellar clouds. The previously reported C_9H_9 laboratory absorption near 628nm is almost certainly due to another species, perhaps incorporating a C5 ring. A search for the *para* form resulted in the discovery of the *p*-ethynylbenzyl radical as a conspicuous product, implying that it may be observable in combustion environments. Along with the indenyl and 1-phenylpropargyl radicals, it is the third isomer of C_9H_7 to have been detected by electronic spectroscopy. Further unambiguous spectroscopic identification of local minima on radical potential energy surfaces is essential for the unraveling of mechanisms of molecular weight growth in combustion.

The PRF award continues to have a substantial positive impact on the PI’s career and on student development. The conclusive identification of C_7H_7 , as well as the work on 1-vinylpropargyl, was reported by the PI at the 2019 International Symposium on Molecular Spectroscopy in Urbana-Champaign. The PI was selected to give a “Hot Topic” talk on C_7H_7 at the recent 2019 International Symposium on Free Radicals in Hangzhou, China. Two of his students presented work on C_5H_5 , C_9H_7 , and C_9H_9 at the same meeting. Experiments on all four works have been completed and manuscripts in preparation. Two students have received research assistantships from the PRF award, and a postdoctoral associate (on PRF support) joined the group in August of this year.

References

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