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DESIGN AND CHEMICAL SYNTHESIS OF IODINE-CONTAINING MOLECULES FOR APPLICATION TO SOLAR-PUMPED I* LASERS

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DESIGN AND CHEMICAL SYNTHESIS OF IODINE-CONTAINING MOLECULES FOR APPLICATION TO SOLAR-PUMPED I* LASERS

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Our work is directed toward the design and chemical synthesis of new media for solar-pumped I* lasers. The rationale for our current efforts is set forth in detail in our recent renewal proposal. In view of the desirability of preparing a perfluoroalkyl iodide absorbing strongly at 300 nm, we have reexamined the relationship between perfluoroalkyl iodide structure and the corresponding absorption wavelength. Analysis of existing data suggests that, in this family of compounds, the absorption maximum shifts to longer wavelength, as desired, as the C-I bond in the lasant is progressively weakened. Weakening of the C-I bond correlates, in turn, with increasing stability of the perfluoroalkyl radical formed upon photodissociation of the iodide. The extremely promising absorption characteristics of perfluoro-tert-butyl iodide can be accounted for on this basis.

Accordingly, we are attempting to achieve even more favorable absorption characteristics, using iodides which will produce particularly stable fluorocarbon radicals upon photodissociation. The greatest stabilization should be attainable in allylic and/or benzylic radicals, which are stabilized by resonance. To test this hypothesis, we first synthesized perfluoroallyl iodide (CF$_2$=CFCF$_2$I, 1), the simplest perfluorinated allylic iodide, and determined the position of its absorption maximum. We initially suggested that this maximum would occur at longer wavelength than the absorption of the corresponding saturated molecule, perfluoro-n-propyl iodide. However, the simple allyl and isopropyl radicals actually are comparable in stability, and on this basis the absorption maxima of CF$_2$=CFCF$_2$I and CF$_3$CF$_2$CF$_2$I are expected to be similar.

We prepared 1 using a published procedure, and found that its max-
mum absorption is at 272 nm. At 266 nm, the perfluoroallyl iodide absorption is ca. twice as strong as that of n-C₃F₇I. Unfortunately, the quantum yield of I* produced in 266 nm photodissociation of the allylic iodide is only 63% (±10%), in contrast to the quantitative generation of I* from several saturated perfluoroalkyl iodide precursors. We tentatively attribute this unexpected result to the competitive formation of electronically excited perfluoroallyl radicals. Whereas perfluoroalkyl radicals possess no low-lying electronic excited states, one or more excited states of the perfluoroallyl radical may be energetically accessible in photodissociation of the iodide, as the excited state energies are lowered by conjugation with the C=C bond. It may be possible to detect these photolysis products experimentally.

A satisfactory test of this interpretation will involve the design and synthesis of a higher homologue of 1, a compound containing additional perfluoroalkyl substituents (e.g., trifluoromethyl groups) on the terminal carbon atoms of the perfluoroallyl iodide moiety. Additional CF₃ groups will further stabilize the radical produced upon photolysis, presumably weakening the C-I bond and shifting the absorption to longer wavelength. The quantum yield of I* from such a precursor will afford important information about the efficiency of I* generation from allylic iodides. Our current target molecule is perfluoro-3-iodocyclopent-1-ene (2). This molecule has not been synthesized previously. We are attempting to prepare 2 from perfluorocyclopent-1-ene (3), which appears to be the only commercially available perfluoroolefin which can afford just a single allylic iodide derivative (i.e., 2). We are presently investigating the reaction of 3 with SO₂, the first of two steps required for the planned synthesis of 2.
In the laboratory of my colleague Stephen R. Leone, a new technique of diode laser probing to obtain precise yields of I* atoms in photodissociation has recently been developed. His co-workers Harold Haugen, Wayne Hess, and Susan Kohler have successfully tuned an InGaAsP diode laser to the six hyperfine transitions of the I atom at 1315 nm. A spectroscopic scan of the absorption transitions taken with this diode laser is shown in Figure 1. The I atoms for this spectrum were produced by thermal dissociation of IBr in a high pressure. Two of the lines are overlapping due to pressure broadening and due to the linewidth of the diode laser itself; nonetheless, all of the relevant transitions can be seen in the diode laser scan. The other unusual feature of this spectrum is that the diode laser was operating at the time on several longitudinal modes with varying intensities in different parts of the spectrum. Thus, the intensities of the lines do not appear to have the proper strengths, but this is just an artifact of the mode structure of the diode laser.

In spite of these minor complications in the operation of the diode laser, it has already been possible to carry out several laser gain-versus-absorption measurements of quantum yields for various iodine-containing compounds, and work is rapidly continuing in these directions. One of the most important measurements to be made was to quantify the yield of excited I* atoms from several standards, n-C3F7I, i-C3F7I, and CH3I at 266 nm. It
is important to point out that there is still a continuing controversy over
the I* quantum yields for these standard compounds. After the work of John
Smedley in Leone's laboratory, there appeared several new works using op-
toacoustic methods which claimed that the quantum yields of the C3F7I com-
pounds were significantly less than unity. The diode laser method has
definitely settled this question. The first measurements show yields for
both C3F7I compounds of 100% and for CH3I of 70%, all at 266 nm
dissociation. The group is currently working to reduce the error bars on
these measurements, which are presently 5%. The tremendous power of the
diode laser technique as a precise probe for I* yields in more exotic com-
pounds and, indeed, also as a diagnostic tool for solar laser media makes
these results some of the most important yet to be developed under this
grant.
Figure 1. InGaAsP Diode Laser Scan over I(2P1/2-2P3/2) Transition: V=1.199 volts, T=17-15°C.

- Multimode operation under these conditions; operative mode is dominant at beginning of scan (left) but is weak at the end (right); fraction of power in "operative" mode decreases from ≈60% to ≈10%
- Utilize multipass in IBr oven at ≈800-900°C; stock has excess I2

![Diagram of energy levels and transitions](image)

Fig. 8. Hyperfine splitting of the iodine-laser transition (after Zuev et al.4).