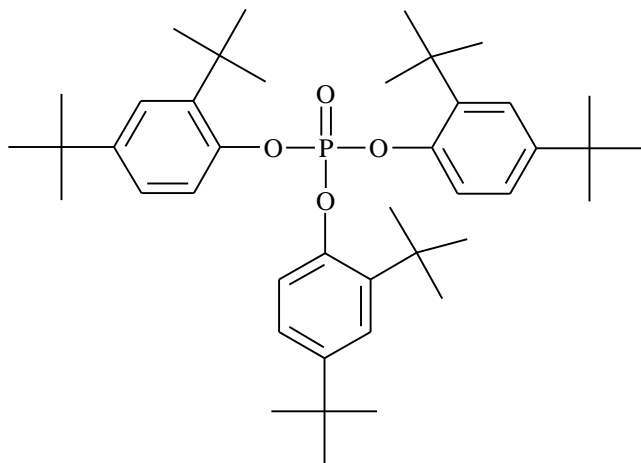


A Very Unusual Doubly Charged Ion in the Mass Spectrum of a Phosphate

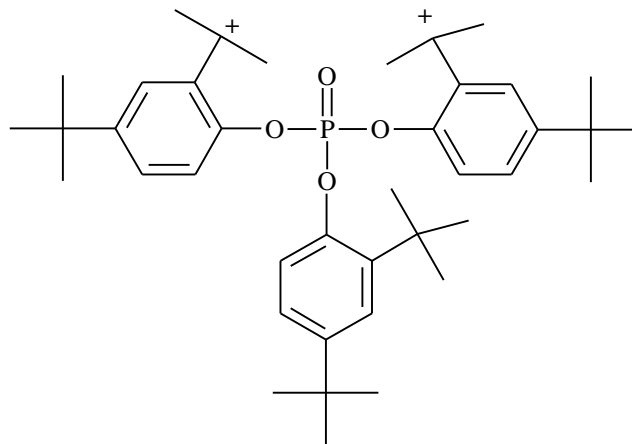
(James Little*, T. Huret, Bob Hale)

Doubly charge ions are often noted in the electron impact mass spectra of many polynuclear aromatics. However, they are usually only present at relatively small intensities. We (T. M. Huret, James Little) noted a very large intensity for m/z 316 in the following phosphate:



Molecular Weight = 662
Molecular Formula = C₄₂H₆₃O₄P

electron impact
↓

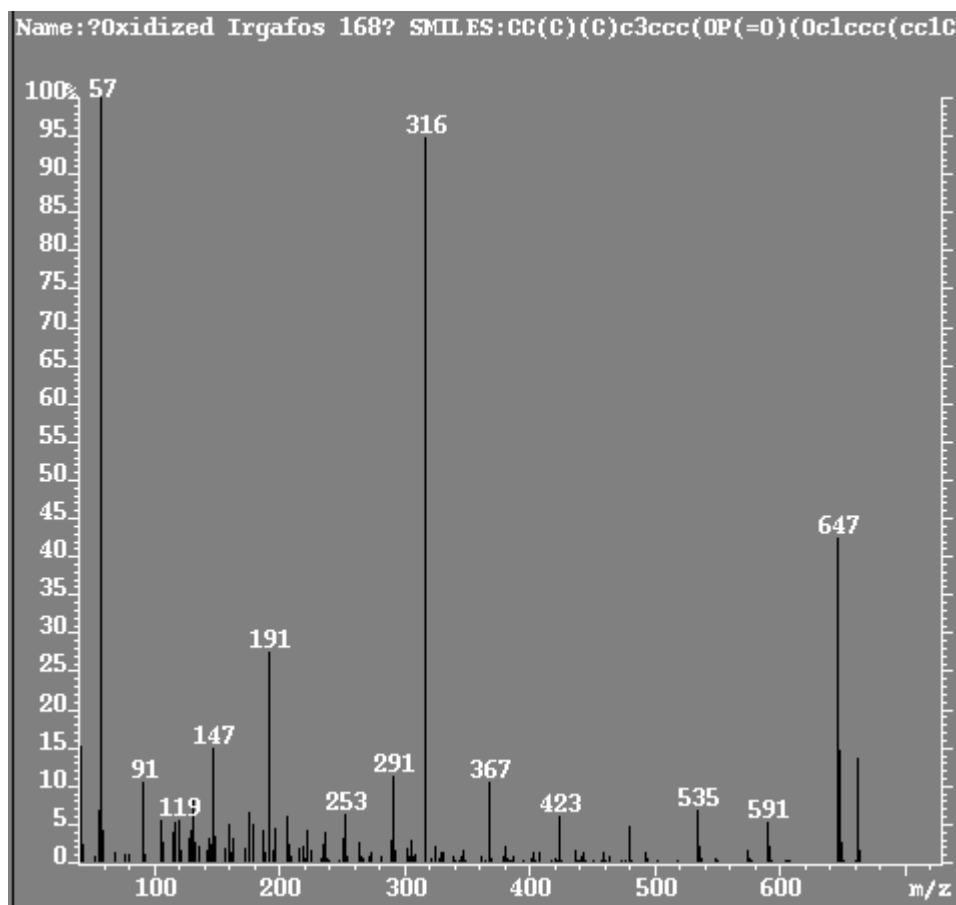


m/z 316

(or isomer with loss of methyls from
different *t*-butyl groups)

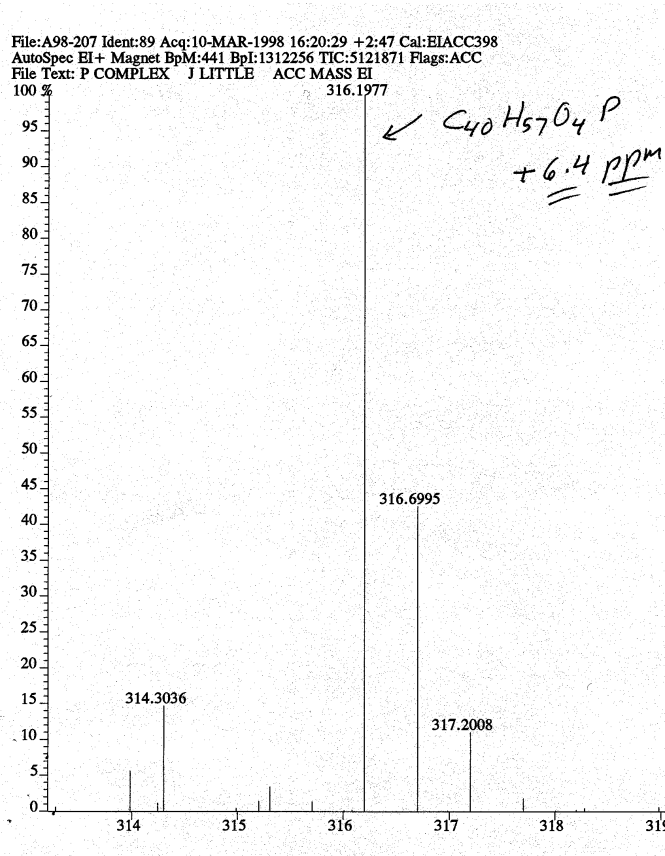
The substructure was confirmed by accurate mass measurements for the doubly charged ion at m/z 316. This required doubling the m/z value to search the standard OPUS elemental composition program ($C_4O_4H_5$, +6.4 ppm error, resolution = 4000). It is interesting to note in the electron impact mass spectrum in the magnetic nominal mass electron impact mass spectrum that no C-13 isotope is observed for the m/z 316 ion even though the instrument is at about 1000 resolution. This is because the data was processed in the merged mode which summed the ion at 316.5 with m/z 316. Thus many doubly charged ions appear to have no C-13 isotopes in many cases because of the data processing mode or lack of adequate resolution on quadrupole mass spectrometers.

Electron Impact Mass Spectrum of Phosphate Showing Large Doubly Charged Ion at m/z 316



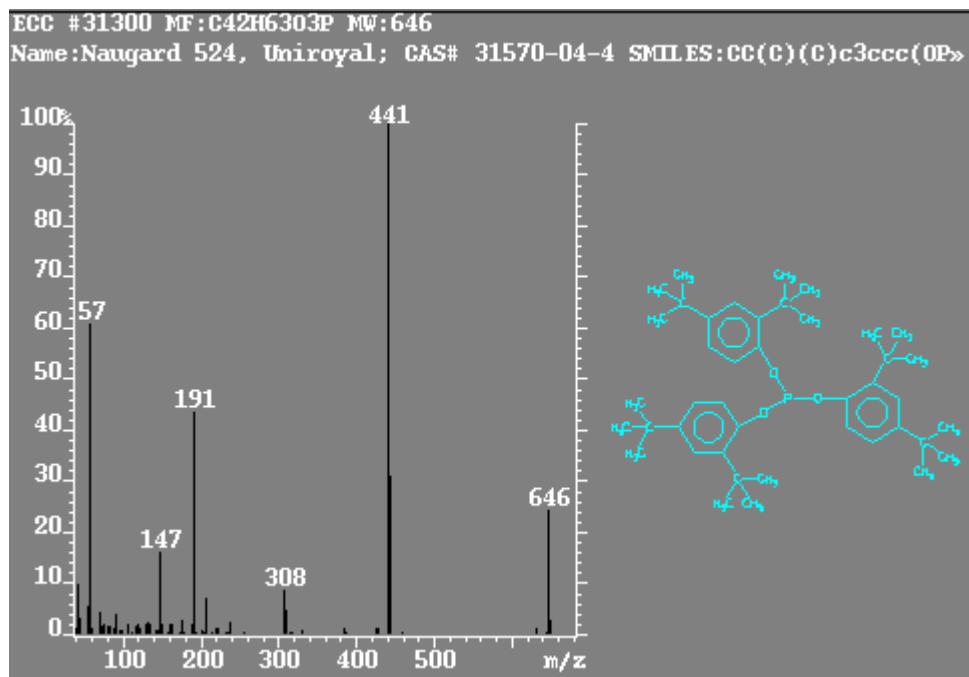
The same spectrum processed in the accurate mass mode shows the presence of the C-13 isotope in approximately the expected ratio at m/z 316.5 in the partial spectrum below:

Expanded EI Mass Spectrum Showing Presence of C-13 Isotope for Doubly Charged Ion



The electron impact mass spectrum of the phosphite of the above compound also shows a doubly charged ion, but at a much lower intensity (m/z 308.2010, +4.1 ppm error, C-13 at 308.7015). Possibly the change of oxidation state from +3 to +5 significantly changes the fragmentation mechanism. The phosphite prefers to lose a phenoxy radical to give m/z 441. The phosphate tends to be singly charged and lose a di-*t*-butylphenoxy radical to yield m/z 441 (see spectrum below).

Electron Impact Mass Spectrum of Phosphite

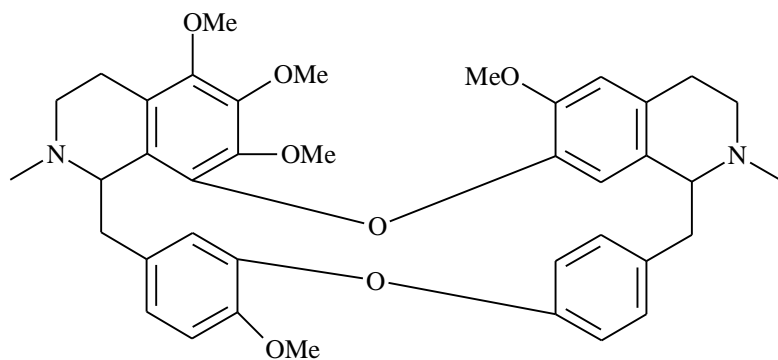


Dr. Fred McLafferty suggested² "...you could postulate that you have a double radical ion, with separate ionization on two of the phenyl groups. The ionization energy of one of these should be almost as low as 8eV, and this resulting charge could be far enough away from a second phenyl group to allow its ionization energy to be surprisingly low. Or you could even try to measure this roughly to show why the doubly charged ion is so prevalent... Anyway, the loss of a methyl radical from a *t*-butyl substituted aromatic ring containing an odd electron of course is totally logical, forming a stable benzyl or propylium ion, with the second methyl radical loss giving you "bis benzyl ion"... Possibly the much lower probability of this double loss reaction from the phosphite is due to the fact that much more electro-negative phosphate does a better job of screening the two phenyls from each other."

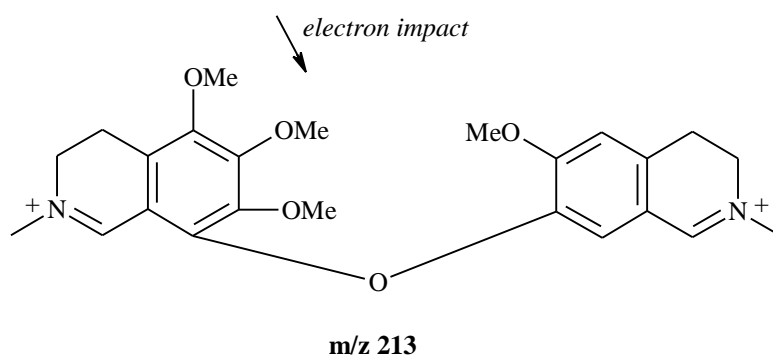
Dr. Kelsey Cook⁴ of the Univ. of TN suggested "I'd bet that there is some kind of rearrangement that ends up with a phosphonium or some such structure, rather than a diradical dication." It is set-up for forming a six-membered ring with one of the ortho-*t*-butyl groups and that might also explain the absence of any triply charged ions.

I found a reference in the literature¹ that cited this unusual doubly charged ion and correctly assigned its structure, but the authors did not find it to be very unusual! The spectrum for the phosphate was not found in either the NIST or Wiley databases.

I shared the spectra with Fred McLafferty² and he sent me another reference³ of an unusual doubly charged ion. The structures for the compound and its doubly charged ion are shown below:



Molecular Weight = 652
Molecular Formula = C₃₉H₄₄N₂O₇



References

1. J. Scheirs, Jan Pospisil, M. J. O'Connor, and S. W. Bigger, *Advances in Chemistry*, 249, Polymer Durability, "Characterization of Conversion Products Formed During Degradation of Processing Antioxidants, pp 360-374.
2. Personal Communication with Fred McLafferty, March 17, 1998.
3. D. C. DeJongh, S. R. Shrader, M. Shamma, B. S. Dudock, M. P. Cava, K. V. Rao, and D. R. Dalton, *Journal of Mass Spectrometry*, Number 1, 1966, p
4. Dr. Kelsey Cook, E-mail, 3/26/99.