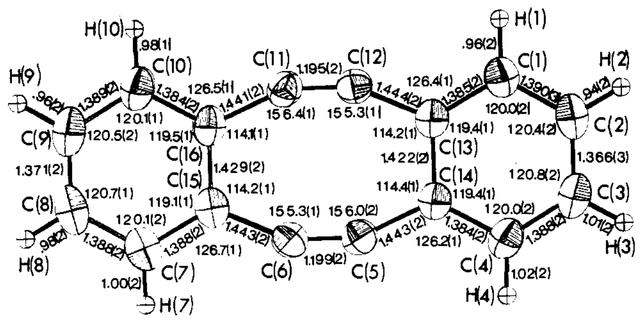

Figure 1. The molecule seen along the direction corresponding to the maximum moment of inertia. The carbon atoms are represented[8] by temperature-factor ellipsoids drawn at the 40% probability level. Hydrogen atoms are on an arbitrary scale.

preliminary structural data are available.[2] The present study provides evidence that the conjugated eight-membered ring of **1** in the crystalline state is substantially planar, the slight deviation from planarity being probably due to intermolecular effects.

Crystals of **1** suitable for diffraction work could be grown from a tetrahydrofuran solution. The compound crystallizes in the monoclinic system with the following unit cell constants: a = 6.144 (1), b = 11.840 (1), c = 14.031 (1) Å; β = 91.01 (1)°; space group $P2_1/n$; Z = 4; ρ_{calcd} = 1.302 g cm^{-3}; μ(Cu Kα) = 5.75 cm^{-1}. The density was not measured, due to the paucity of the substance in our hands after crystallization. A complete set of diffraction maxima within a θ sphere of 70° was measured with a fully automated four-circle diffractometer using Cu radiation [λ(Cu Kα) = 1.5418 Å; graphite monochromator] and a variable rate θ–2θ scan technique. A single standard check reflection was measured after every 15 reflections; a general downward trend in the intensity of this reflection was observed, the intensity drop at the end of the data collection amounting to 10%. Of the 1910 reflections measured a total of 1775 were judged observed after correction for Lorentz, polarization, background, and decay effects. The structure was solved by automated interpretation[3] of the Patterson function. Least-squares refinement using anisotropic thermal parameters for carbon atoms, isotropic temperature parameters for hydrogen atoms, an overall scale factor, and a secondary extinction parameter[4] gives a value of the conventional R index[5] of 0.048 and a weighted R index[6] of 0.050. The refined atomic coordinates are given in Table I;[7] observed and calculated structure factors are listed in Table II.[7]

A drawing of the molecule is shown in Figure 1, which includes bond distances and angles involving C atoms and C–H distances.[8] For sake of clarity the values of the C–C–H angles have not been reported; they range between 118 and 121° (esd's = 1°).

Four structural features are of special note. (1) The average value of the angles at carbon atoms involved in triple bonds is 155.8° (to be compared with a value of 159.1° in **2** and of 158.5° in cyclooctyne[9]). (2) The distance between the triple bonds is 2.61 Å (against 2.57 Å in **2**). (3) Atoms C(5), C(6), C(11), and C(12) are coplanar within 0.001 Å (plane A); the displacements of the other four atoms of the eight-membered ring from plane A range between 0.014 and 0.023 Å, all in the same direction. (4) The two outer benzene rings are planar within experimental uncertainty (maximum deviation 0.003 Å); their planes are both folded out of plane A, on the same side, by about 2°. This folding, and the consequent nonstrict planarity of the central ring, can presumably be ascribed to packing interactions. Among these, we notice a rather short contact of 3.45 Å, which involves atom C(1) and atom C(8) of another molecule at $1 - x, -y, 1 - z$; a less critical contact of 3.54 Å implicates atom C(14) of the first molecule and atom C(10) of the molecule transformed as for C(8).

Acknowledgments. The authors feel especially indebted to Professor F. Sondheimer, who kindly supplied them with the crystal specimens prior to the publication of his paper.[1]

Supplementary Material Available. A listing of final atomic parameters and structure factors will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-75-658.

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Riccardo Destro, Tullio Pilati, Massimo Simonetta*
Istituto di Chimica Fisica e Centro C.N.R., Università
20133 Milan, Italy

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Correlation between Proton Affinity and Core-Electron Ionization Potentials for Double-Bonded Oxygen. Site of Protonation in Esters

Sir:

A striking correlation of the proton affinities of a number of alcohols and amines with the core-electron ionization potentials of oxygen or nitrogen in the same molecule has been pointed out by Martin and Shirley[1] and by Davis and Rabalais.[2] The change in proton affinity from one molecule to another is almost exactly equal to the change in core ionization potential. The reason for this result is that the removal of a core electron from the oxygen or nitrogen is electrically equivalent to the addition of a proton at the same site. It was suggested by Martin and Shirley that the ionization-potential shifts and proton affinities might be comparable over a wider range than they had considered.

Davis and Rabalais found, however, that the point for acetone fell off of their correlation line by about 1 eV and that the point for formic acid was off by nearly 0.5 eV. They concluded, therefore, that double-bonded oxygen does not fit the correlation and proposed a number of reasons to account for the phenomenon.

We have recently remeasured the oxygen 1s ionization potential in acetone to be 537.92 eV, in substantial disagreement with the previously reported value of 539.0 eV.[3] Our new value falls quite close to the correlation line for the alcohols. In addition, we have measured oxygen 1s ionization potentials for methyl acetate (537.87 and 539.43 eV), formaldehyde (539.42 eV[4]), and acetaldehyde (538.62 eV[5])

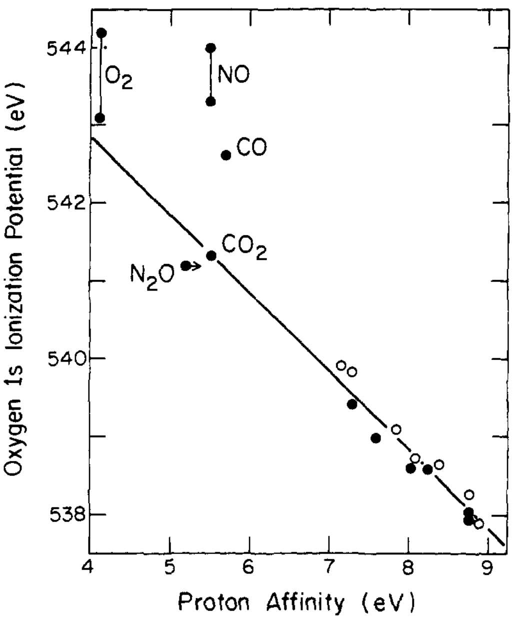

Figure 1. Correlation of oxygen 1s ionization potentials with proton affinities. Open circles represent data previously discussed in ref 1 and 2. Filled circles represent new results. The unlabeled solid circles in the lower right represent, from top to bottom, H_2CO, HCOOH, CH_3CHO, $(CH_3)_2O$, CH_3COOCH_3, and $(CH_3)_2CO$. The open circles represent, from top to bottom, H_2O, CF_3CH_2OH, CH_3OH, CH_3CH_2OH, $(CH_3)_2CHOH$, $(CH_3)_3COH$, and $(C_2H_5)_2O$. For carboxyl oxygens only the lower of the two ionization potentials has been used. The proton affinity for N_2O has been reported only as a lower limit.

and have remeasured this quantity for formic acid (538.92 and 540.60 eV[6]). These ionization potentials also fall quite close to the same correlation line.[7]

We have extended this comparison of proton affinities and inner-shell ionization potentials by considering O_2, NO, CO_2, CO, and N_2O—rather different molecules from those previously considered—together with a recent measurement we have made on methyl ether.[8]

The correlation of proton affinity with core ionization potential is shown in Figure 1. The data previously presented by Martin and Shirley and by Davis and Rabalais are shown as open circles, the additional results[9] mentioned above as filled circles. The line is a least-squares fit, constrained to a slope of -1, to all of the data except those for CO, NO, N_2O, and O_2, and corresponds to the relationship IP(1s) + PA = 546.84 eV. We see that, except for the diatomic molecules, all of the points fall within about 0.2 eV of the line, in agreement with the suggestion made by Martin and Shirley that this relationship should hold for a wide class of compounds. Even the diatomic molecules, although falling farther off the line, are in agreement with the general trend.

A closer inspection of the data shows that the points for the double-bonded oxygen fall consistently lower than those for single-bonded oxygen. If these data are fit separately with lines of slope = -1, these are displaced from one another by 0.25 eV. The root-mean-square deviation of the points from their respective lines is about 0.1 eV, which is comparable to the experimental error in the measurement of both proton affinity and core ionization potential. This slight difference between the two kinds of oxygen may, as has been pointed out by Davis and Rabalais, arise from the different hybridization involved in single and double bonds.

For formic acid and methyl acetate there are two oxygen 1s ionization potentials, one for the keto oxygen and one for the ether oxygen. The lower of these correlates well with the proton affinity; the higher falls about 1.5 eV above the line. Protonation evidently occurs at the oxygen with the lower 1s ionization potential. Inspection of the other data reveals that keto oxygens have lower core ionization potentials than do ether oxygens in similar compounds. The molecular orbital calculations of Snyder and Basch[10] predict that the keto oxygen in formic acid will have the lower ionization potential. Combining these observations we conclude that protonation occurs at the keto oxygen. This conclusion is the reverse of that reached by Pesheck and Buttrill[11] from ion-cyclotron-resonance results.

We have mentioned above new results and remeasured results for oxygen 1s ionization potentials. These were measured on mixtures of the gas of interest with either carbon dioxide or carbon monoxide as a reference compound so that any drifts in the spectrometer focusing voltage were compensated. The oxygen 1s ionization potential in carbon dioxide is accurately known, having been measured independently in separate laboratories to be 541.32 ± 0.05[12] and 541.28 ± 0.12 eV.[13] We have recently remeasured the oxygen 1s ionization potential in carbon monoxide to be 542.58 eV,[14] somewhat higher than previously reported values.[3,15]

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T. X. Carroll, S. R. Smith, T. D. Thomas*
Department of Chemistry and Radiation Center
Oregon State University
Corvallis, Oregon 97331

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Resonance Raman Studies of Nitric Oxide Hemoglobin

Sir:

Resonance Raman scattering from a variety of heme proteins has recently been investigated.[1-3] If the laser wave-