The Buta-1,3-diene-1,4-sultone (Pysultone) Ring, a Non-aromatic 6π-Electron System: *X*-Ray Structural Determination

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Summary The first *X*-ray structure of a pysultone ring indicates the ring is a non-aromatic 6π-electron system.

Aromatic character in various systems having $4n + 2$ peripheral π-electrons is of continuing interest.[1] A variety of criteria have been employed as evidence for aromaticity including chemical reactivity,[2] ring current,[3,4] diamagnetic susceptibility,[5] and *X*-ray structural evidence.[4,6] In this paper, we report results of the first *X*-ray structural analysis of a pysultone ring.† These results support the conclusion that pysultones are not aromatic.[7,8]

Crystals of the pysultone (**1**)[9] were grown from ethyl acetate–hexane. Precession photographs were recorded for a crystal using Mo-K_α ($\lambda = 0{\cdot}7107$ Å) radiation. The crystal was monoclinic; systematic absences along $0k0$ ($k = 2n + 1$) and on $h0l$ ($l = 2n + 1$) uniquely identified the space group $P2_1/c$. The needle axis, along which the crystal was mounted, was the non-unique axis *a*. Lattice

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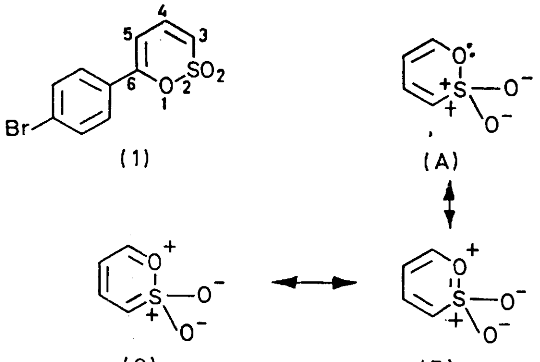
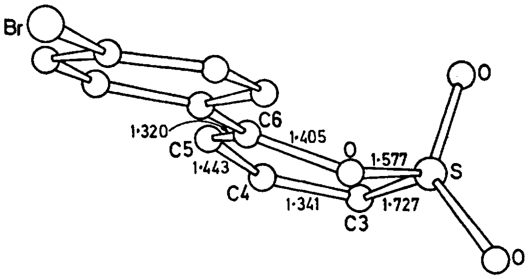
† The sulphur containing ring in (**1**) has the systematic name, buta-1,3-diene-1,4-sultone. We prefer the shorter trivial name pysultone which is related to the name of corresponding lactone, α-pyrone.

constants were measured from the diffractometer by least-squares fit of observed angles: a = 7·52, b = 10·00, c = 14·08 Å; β = 91·32°; D_m = 177 g cm^{-3}, D_c = 1·80 g cm^{-3} for Z = 4.



The structure was solved initially by the heavy-atom method[10] using visually estimated Weissenberg film data (1095 unique non-zero reflections). Least-squares refinement of the film data converged to a conventional R = 0·143. Diffraction maxima were later remeasured on an Enraf–Nonius automated diffractometer (CAD-3). In all, 1366 unique non-zero reflections were considered to be above background and used in the analysis. Weighted full-matrix least-squares refinement of the atomic position parameters and anisotropic temperature factors for all non-hydrogen atoms using diffractometer data reduced R to 0·07. Standard deviations for C–O and C–C bond lengths average 0·012 Å; standard deviations for S–C and S–O bond lengths average 0·007 Å. All bond angles have standard deviations of less than 0·9°. No hydrogen atoms have been included in the refinement at this point.

Structural features (see Figure) of special interest are (i) the near coplanarity of the phenyl ring with a mean plane through the pysultone ring, (ii) the 0·58 Å deviation of the sulphur atom out of a plane formed by O, C(4), C(5), and C(6) within the sultone ring,‡ and (iii) the alternating lengths of carbon–carbon sp^2 bonds in the pysultone ring. The carbon–carbon bond between C(4)–C(5) is 1·443 Å (e.s.d. = 0·012), indicative of considerable single bond character since the mean values for carbon–carbon single, double, and aromatic sp^2–sp^2 bonds are 1·47, 1·34, and 1·40 Å, respectively.[11] The C(3)–C(4) bond, 1·341 Å (e.s.d. = 0·014 Å) and the C(5)–C(6) bond, 1·320 Å (e.s.d. = 0·012 Å) have considerable double bond character. These experimental facts support the idea that resonance contributors of the type A and B accurately describe a pysultone ring. Minor contributions from such resonance structures as C are consistent with the concept of a non-aromatic ring system having localized alternating double and single bonds.



FIGURE

The discovery that pysultones are not aromatic is in contrast with the work of Weil.[8] Our findings are in agreement with the discovery by Mock, *et al.*[6,12] that the structurally related thiepin 1,1-dioxide is a non-aromatic 6π-electron, boat-shaped molecule.

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‡ O, C(4), C(5) and C(6) are essentially coplanar (± 0·003 Å deviations from the best calculated plane); C(3) and S are 0·212 and 0·578Å below the plane respectively.

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