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X-Ray Crystal Structure of an Ozonide: 4-(4-Nitrophenylmethyl)-1-phenyl-1,4-epoxy-1*H*-2,3-benzodioxepin-5(4*H*)-one

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Summary X-Ray analysis of a single crystal of 4-(4-nitrophenylmethyl)-1-phenyl-1,4-epoxy-1*H*-2,3-benzodioxepin-5(4*H*)-one has elucidated the first unambiguous crystal structure of an ozonide.

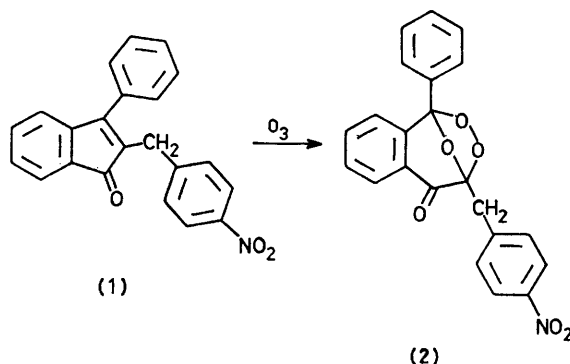
CRIEGEE has shown that ozone reacts with some olefinic compounds to form primary ozonides having the 1,2,3-trioxolan structure.¹ These primary ozonides then rearrange and/or dissociate to form ozonides which had been shown previously by Rieche² to have the 1,2,4-trioxolan structure. Prior to this work, the molecular structure of any ozonide had not been unambiguously established to our knowledge by single crystal X-ray analysis. Previous structural studies include investigations by electron diffraction of ethylene ozonide^{3,4} and microwave analysis for ethylene,⁵ propene and *trans*-but-2-ene ozonides.⁶ The structure of 3-methoxycarbonyl-5-anisyl-1,2,4-trioxacyclopentane was investigated by X-ray diffraction; however, the geometry of the 1,2,4-trioxolan ring could not be established because of structural disorder.⁷

In connection with our interest in the stability of ozonides, we have established the structure of the epoxy benzodioxepinone (2) by single crystal X-ray diffraction. This particular *para*-substituted compound has shown exceptional stability and hence was chosen for this work.⁸

A solution of the indenone (1) (1.284 mmol) in dry methylene chloride, cooled to 0 °C, was treated with an oxygen-ozone mixture to give the benzodioxepin (2). Recrystallization from methanol gave colourless crystals (66.9% yield), m.p. 106–107.5 °C, i.r. (CH₂Cl₂) 1719, 1600, 1350, and 1200 cm⁻¹, n.m.r. δ (CDCl₃; 60 MHz) ArH (6.8–8.3) (13H) and CH₂ (AB pattern, 2.79 and 2.63, *J* 9.9 Hz).

Crystal data: Crystals of C₂₂H₁₅NO₆ are monoclinic, space group *P*2₁/*c*, *a* = 8.205(9), *b* = 14.585(7), *c* = 15.925(5) Å,

β = 100.05(8)°, and *Z* = 4. Data were collected on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator. Least square refinement of 25 centred reflections produced an orientation matrix for data collection as well as the cell constants. Data were collected in the range 4° < 2 θ < 50° using Mo-K α radiation, λ 0.71069 Å. Two standard reflections were monitored every 2 h to check crystal stability. No significant variation in intensity or position was noted. A total of 1150 reflections, with *I* > 3 σ (*I*), were used in the refinement utilizing a crystallographic least square programme.⁹



The data set was corrected for Lorentz and polarization factors but an absorption correction was not applied. After full matrix least square refinement of the non-hydrogen positional and anisotropic thermal parameters, the final *R* value was 5.15%. All the hydrogen atoms were located in a difference Fourier map and held constant in the refinement. The final view of the molecule is shown in the Figure.

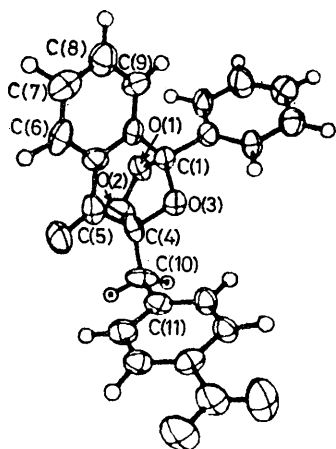


FIGURE. ORTEP drawing of $C_{22}H_{16}NO_6$ (2).

The *X*-ray study reveals the presence of a five-membered ring in an epoxide-oxygen envelope configuration. Although microwave studies^{5,6} as well as conformational analysis^{10,11} indicate this to be the least stable configuration (the oxygen half-chair and carbon-epoxide oxygen half-

chair being more stable), the epoxide-oxygen envelope configuration appears to be the only one possible for the molecule.

The bond distances and angles of the five-membered ring [C(4), O(3), C(1), O(1), O(2)] are: C(4)-O(3), 1.406(9); O(3)-C(1), 1.435(9); C(1)-O(1), 1.466(9); O(1)-O(2), 1.459(7); and O(2)-C(4), 1.473(9) Å; \angle C(4)-O(3)-C(1), 104.6(7); \angle O(3)-C(1)-O(1), 101.8(7); \angle C(1)-O(1)-O(2), 106.3(6); \angle O(1)-O(2)-C(4), 104.8(6); \angle O(2)-C(4)-O(3), 103.3(7)°.[†]

Comparison of the data from this study with the data from the propene ozonide study⁶ indicates some difference in the C(1)-O(1) and O(2)-C(4) bonds. Whereas the bond lengths in the indenone ozonide are 1.466 and 1.473 Å, respectively, the same bonds in propene ozonide were determined by microwave studies to be 1.399 and 1.411 Å. This could be attributed to the significant structural differences in the starting substituted ethylenes with rigid substituent constraints existing in the indenone.

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[†] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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