Notes

The X-Ray Crystal and Molecular Structure of an Unusually Stable Cyclic Organic Peroxide

J. N. Brown*

Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616

R. L. R. Towns, M. J. Kovelan, and A. H. Andrist*

Department of Chemistry, The Cleveland State University, Cleveland, Ohio 44115

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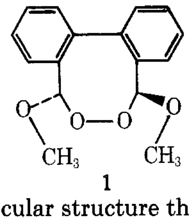
While the organic peroxides are an ubiquitous class of compounds whose chemical reactivity is relatively well known, the natural variations in peroxide structural parameters and resulting structure–reactivity correlations have yet to be fully enumerated. This paucity of structural data may reflect on their inherent thermodynamic instabilities as well as difficulties encountered in their handling.

In striking contrast to this reactivity norm is the thermally stable (e.g., mp 180–181 °C before decomposition) dimethoxy peroxide 1 produced in the acid-catalyzed methanolysis of phenanthrene ozonide.[1,2] Although dihydroxyalkyl peroxides have been isolated from equilibrium mixtures of aldehydes and hydrogen peroxide,[3] and dimethoxyalkyl peroxides have been prepared through alkene ozonolysis reactions in methanol,[4] no members of the two series exhibit the thermal stability characteristic of 3,8-dimethoxy-4,5,6,7-dibenzo-1,2-dioxacyclooctane (1). The structure of peroxide 1, exclusive of the stereochemical relationship between the methoxy groups, was initially proposed on the basis of its infrared spectrum, C–H analysis, and molecular weight determinations.[1] This proposal has recently been strengthened with natural abundance ^{13}C and ^{1}H NMR spectra as well as mass spectral data.[4,5] In order to confirm these conclusions, determine the stereochemistry of the methoxy groups, and gain insight into the unusual stability of peroxide 1 we have fully determined its molecular structure through a single-crystal x-ray diffraction study.



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Experimental Section

3,8-Dimethoxy-4,5,6,7-dibenzo-1,2-dioxacyclooctane (1) was prepared through ozonolysis of phenanthrene in methanol at −30 °C as described by Bailey.[1,2] After recrystallization from chloroform, a needle-shaped crystal, 0.3 mm in length and 0.1 mm in diameter, was mounted on a glass fiber in air with the [*h*0*h*] direction coincident with the ϕ axis of a Picker FACS-I four-circle diffractometer. The reciprocal lattice showed $C2/m$ symmetry with systematic extinctions $l = 2n + 1$ for all reflections, which is consistent with space groups $C_{2/c}$ and C_c. The centrosymmetric $C_{2/c}$ was chosen and the choice was justified by the subsequent refinement. Lattice constants were determined at 25 °C by a least-squares fit of 12 carefully measured 2θ values of the Cu Kα_1 and Kα_2 doublet for reflections with $2\theta > 60°$. The resultant lattice constants and their estimated standard deviations are $a = 10.209$ (1), $b = 13.322$ (1), $c = 11.937$ (1) Å, and $\beta = 122.76$ (1)°. The observed density, 1.31 g/cm^3 (by a flotation method using chloroform and 2-butanone), agrees with the calculated density, 1.32 g/cm^3, assuming four peroxide molecules per unit cell.

Intensity data were collected on a Picker FACS-I fully automated diffractometer using Ni-filtered Cu Kα radiation. A θ–2θ scan rate of 2°/min, with a variable scan width (2.3° ± 0.4° tan θ) and 10-s background measurements at the extremities of the scan, were used to measure the 1093 unique reflections to a 2θ maximum of 125° ($d = 0.87$ Å). The intensities were corrected for Lorentz–polarization effects and absorption as a function of ϕ, with a transmission factor of 1.06:1.00 (linear $\mu = 7.9$ cm^{-1} for Cu Kα radiation). During the 28 h of actual x-ray exposure, the crystal exhibited an extreme intensity decay as monitored by three standard reflections measured hourly. Although the decay appeared anisotropic, the intensities were corrected for an isotropic linear decay of 40%. Structure amplitudes were calculated and a total of 891 (81%) reflections were considered statistically significant by the criterion $|F| > 3\sigma(F)$.

Structure Determination. The structure was solved by direct methods. After conversion to normalized structure magnitudes ($|E|$'s) with appropriate scaling using a k curve,[6] 130 reflections with $|E| \geqslant 1.50$ were obtained. An origin was selected by specifying the phases of two reflections. The phases of five other reflections were permuted resulting in 32 combinations, using the program MULTAN.[7]

An E map, calculated for the most consistent set, contained the ten unique nonhydrogen atoms among the top 12 peaks consistent with the expected structure. The molecule possesses a twofold axis of rotation (position e). Ten cycles of block-diagonal, least-squares isotropic refinement using $1/\sigma^2$ weights resulted in a value of the reliability index, $R = 0.14$.[8]

After conversion to anisotropic temperature factors, refinement was continued for ten more cycles, resulting in a value of $R = 0.10$. Since a difference electron density map at this stage showed no peaks greater than 0.3 e/Å^3, the coordinates of the five nonmethyl hydrogen atoms were calculated from expected geometry and included in future structure factor calculations but not refined. The refinement converged to a final value of $R = 0.077$ with the shifts in all parameters being significantly less than one-tenth of the estimated standard deviation of the respective parameter. The standard deviations of the bond distances, given in parentheses for the least significant figure, were calculated using the standard deviations of the xyz coordinates only.

Results and Discussion

Figure 1 shows the observed bond distances and angles as well as the atom labeling scheme. Figure 2 is an ORTEP[9] stereoscopic drawing of the complete molecule. The bond distances and bond angles in the aromatic rings are normal (1.398 ± 0.006 Å and 120.0 ± 0.9°, respectively). The dihedral angle between the aromatic rings is 61.9°. Figure 2 also clearly illustrates the fact that the methoxy groups are trans to one

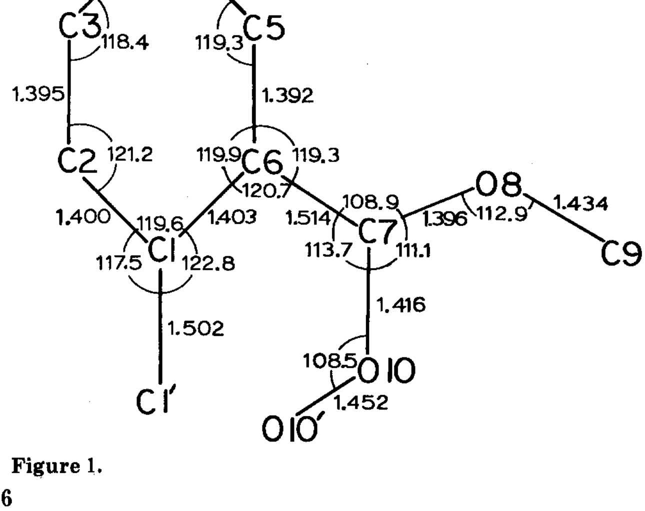


Figure 1.

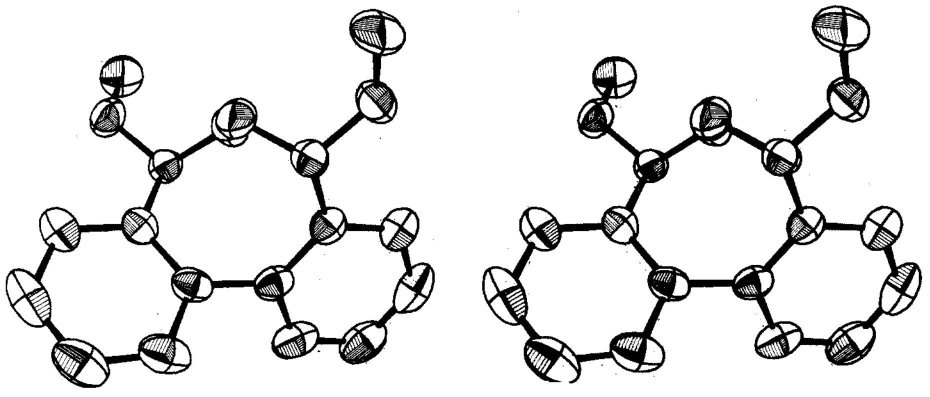
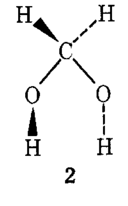


Figure 2.

another, a fact consistent with but not deducible from the spectroscopic studies.[2,5] The peroxide O10–O10′ bond [1.452 (18) Å] is shorter than those reported (1.48 Å) for dimeric and trimeric alkyl ketone peroxides[10–12] accounting, at least in part, for the unusual thermal stability of **1**. The C–O distance in the eight-membered ring is 1.416 (17) Å and is comparable to that observed in trimeric acetone peroxide.[10] The methyl C–O in the methoxy group compares with that observed in other studies,[13] but the Me–O–C angle (110°) is significantly compressed. The C–O–C angles within the eight-membered ring (108.5°) are consistent with those observed in the di- and trimeric alkyl ketone peroxides. The closest intermolecular contact distance is 3.37 Å observed between C3 and O10 in the molecule related by $\frac{1}{2} + x, \frac{1}{2} + y, z$.

The ab initio self-consistent field molecular orbital calculations carried out on methanediol by Radom, Hehre, and Pople[14] provide a useful theoretical framework for understanding the structural details of peroxide 1.

Pople and co-workers found that of a series of 48 saturated molecules, methanediol possessed the largest "bond separation energy" (15.2 kcal mol^{-1}), or, in other words, the largest positive heat of reaction in its theoretical conversion along with 1 mol of methane to 2 mol of methanol. Therefore, since the bond separation energies evaluate the interactions between various bonds in terms of back-donating $n \rightarrow \sigma^*$ electron transfer, the Pople calculations[14] determined that this bond-strengthening interaction is strongest between the two C–O bonds of methanediol. It was further determined that this interaction has its greatest effect when the OCO plane is perpendicular to the COH plane. This leads to a favorable orientation of dipoles for the two OH groups within the preferred double gauche conformation, **2**.[14]



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Perhaps these same orbital interactions account for the unusual stability of peroxide 1 through strong $n \rightarrow \sigma^*$ back-donation of electron density into the peroxide bond from the geminal C–O bonds on the adjacent atoms (C7 and C7′). The double gauche conformation is indeed evident about C7 and C7′. The trends in bond lengths also strengthen the validity of the methanediol theoretical model: $n \rightarrow \sigma^*$ back-donation alternately lengthens C9–O8 [1.434 (10) Å], shortens O8–C7 [1.396 (12) Å], lengthens C7–O10 [1.416 (17) Å], and shortens O10–O10′ [1.452 (18) Å].

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Supplementary Material Available. Tables of temperature and structure factors may be obtained upon request from the authors. The observed fractional coordinates for the unique atoms in the molecule have been retained as supplementary material for the microfilm edition (1 page). Ordering information is given on any current masthead page.

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A Novel Route to 1-Aminoalkylphosphonic Acids

Wojciech J. Stec* and Krystyna Lesiak

Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, 90-362 Łódź, Boczna 5, Poland

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In view of the increasing interest in the biological[1] and chelating[2] properties of 1-aminoalkylphosphonic acids and 1-aminoalkylphosphine oxides we wish to report a convenient new route for the synthesis of these important classes of compounds. Recently we described a simple synthesis of *O,O*-diethyl 1-[*N*-ethoxycarbonylimino]-1-thioethyl methylphosphonate (**1a**) and its reaction with sulfuryl chloride to give **1b**.[3]