Synthesis and Characterization by *X*-Ray Crystallography of a Triphenylene Triepoxide

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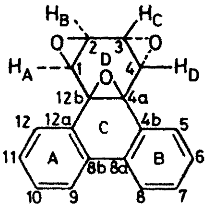
Summary The synthesis, by direct oxidation, and characterization, by *X*-ray diffraction techniques, of an unsymmetrical triepoxide of triphenylene are described.

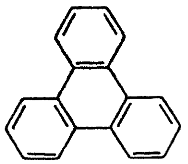
Recently, it has become increasingly apparent that the main activation of polynuclear hydrocarbons into carcinogens proceeds *via* enzymatic oxidation to give arene oxides capable of covalent binding to key cellular sites.[1] During our studies[2] on the direct oxidation of aromatic systems into oxirans which are potentially useful in metabolic studies, we have synthesized a triepoxide (**1**) derived from triphenylene (**2**).

Oxidation of (**2**) with *m*-chloroperbenzoic acid (6—20 equiv.) in a two-phase system (organic phase, CH_2Cl_2; aqueous phase, saturated aqueous $NaHCO_3$) which is vigorously stirred for 2—5 h gives (**1**) in a yield (10—55%) which is dependent on the substrate concentration as well as on the amount of peracid used.[3] The epoxide (**1**) is obtained in a pure state by elution in 100 ml fractions from an alumina column (25 mm × 40 cm, Woelm neutral DCC alumina, act. III), with absolute diethyl ether. The first fraction contains the starting material (**2**) and traces of a carbonyl-compound (**3**), and (**1**) is in the third and fourth fractions. Further elution with methanol gives a phenolic product in low yield.

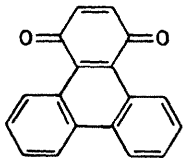
Reduction of (**1**) with an excess of Ti^{II} (McMurry's reagent[4]) gives (**2**) and traces of the phenol (**4**), which ensures that no skeletal rearrangement accompanies oxidation and subsequent purification. The phenol (**4**) is assumed to arise



(1)



(2)



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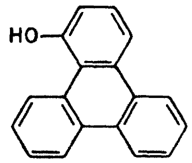
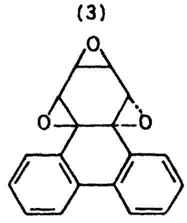


(4)



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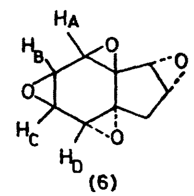
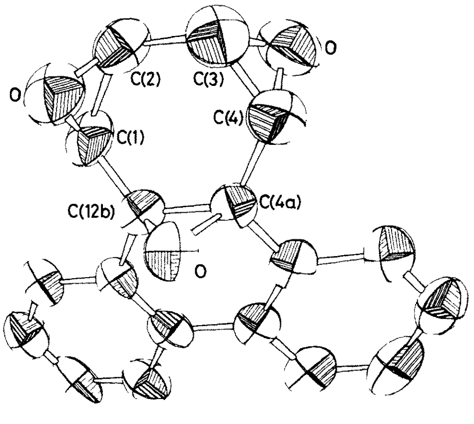


(6)

from a monoepoxide by a mechanism analogous to the NIH shift [5] Hydrolysis of (**1**) followed by periodic acid-oxidation gives a product identical to an authentic sample of diphenic acid indicating that oxidation is confined to one fused-ring of the system

The mass spectrum (EI 70 eV) of the triepoxide (**1**)[212 °C (sealed tube under N_2)] exhibits a parent peak at m/e 276 (M^+) and additional significant fragments signals at m/e 260, 247, 218, and 189 The i r spectrum shows weak bands at 885, 1205, and 1450 cm^{-1} and signals in the carbonyl-region are conspicuously absent The u v spectrum is characterized by an absorption band at λ_{max} 276 nm (ϵ_{max} 9·3 × 10^3, EtOH) and the spectral pattern resembles that of phenanthrene rather than biphenyl This evidence, along with the planes calculations (*vide infra*), demonstrates that there is substantial planar-aromatic character exhibited by the two phenyl-rings in (**1**), unlike biphenyl where the angle between the ring systems is 41 6 ± 2 0° [6] The 90 MHz ^{1}H [δ (Me$_4$Si) 3 56 (dd, H^B), 3 74 (ddd, H^C), 4 1 (dd, H^A), 4 3 (d, H^D), 7 4—7 6 (m, 6-, 7-, 10-, and 11-H), and 7·95—8·25 (m, 5-, 8-, 9-, and 12-H)] and 22 63 MHz ^{13}C n m r spectra [δ (Me$_4$Si) 58·8 and 58 3 (s) (C-4a and -12b), 51·8 (d), 50·7 (d), 49 4 (d), and 48 1 (d) p p m , $^1J_{C-H}$ for C(1—4) 160 ± 4 Hz] preclude the presence of a plane of symmetry or a C_2 rotational axis The n m r evidence shows that the stereochemical assignment for (**1**) is correct and the alternative unsymmetrical structure (**5**) may be excluded A $^3J_{BC}$ coupling-constant of 1 2 Hz is observed in the spectrum of (**1**) whereas the analogous value reported for the perhydroindene tetraepoxide (**6**),[7] a model for (**5**), is 3·7 Hz ^{1}H–^{1}H Spin-decoupling experiments show that the proton at δ 4 3 is *vicinal* to the proton resonating at δ 3 74, as is the case for the remaining two epoxide-proton signals (δ 4·1 and 3 56) These observations are inconsistent with the assignment of structure (**5**) to the triepoxide Attempts to assign specific resonances to H-1, H-2, H-3, and H-4 unambiguously using n m r techniques proved difficult Because of this structural ambiguity, a three-dimensional X-ray crystallographic study of (**1**) was undertaken

Crystal data C$_{18}$H$_{12}$O$_3$, monoclinic, space group $P2_1/c$, $a =$ 8·866(2), $b =$ 18·726(3), $c =$ 7 912(1) Å, $\beta =$ 107 0(2)°, $Z = 4$ A total of 854 reflections were considered as statistically significant based upon the criterion $(I_{Ni} - 2\sigma I_{Ni}) - (I_{Co} - 2\sigma I_{Co}) > 100$, where σ is based on counting statistics Stationary counter-stationary crystal techniques were used on an automated G E XRD-490 system using Cu-K_α radiation to $2\theta = 120°$ The structure was solved by direct methods† and refined in the usual way (anisotropic temperature factors for non-hydrogen atoms, isotropic for hydrogen) to the present R factor of 9·1% The Figure shows that the structure is indeed the same as (**1**) ‡ A least-squares fit of various atoms to planes show that the only planar regions (within an e s d of 0 01 Å) are each of the two phenyl-rings Taken together, these 12 carbons are not planar (best combined least-squares plane has an e s d of 0 05 Å) with the individual phenyl-rings at 174° to each other and hence are twisted 6° away from planarity, presumably to avoid interaction of the hydrogens attached to C-8 and C-9 Although rings C and D only approximate planarity (e s d of 0 03 and 0·04 Å, respectively), the dihedral angle between them, 158 4°, is consistent with a previously reported value of 155·6°[8] for the pentaepoxide of naphthalene §



FIGURE

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† The conventional reliability index $R = \Sigma|KF_0| - |F_c|/\Sigma|KF_0|$ is cited in the paper Scattering factors for carbon and oxygen are taken from the paper by D T Cromer and J T Waber, *Acta Crystallogr* 1965, **18**, 104, while that for hydrogen is from 'International Tables for X-ray Crystallography,' Vol III eds N F M Henry and K Lonsdale Kynoch Press, Birmingham, 1968 The programs used are part of the crystallographic package for the PDP-10 developed at U N O by J N Brown, R L Towns, R J Majeste, and L M Trefonas (1976–1977) The package includes a series of direct-methods programs (among them, FAZC for centrosymmetric crystals and MULTAN II for general cases)

‡ 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

§ Although the crystallographic study for one of the triepoxides of benzene has also been reported (W Littke and U Druck, *Angew Chem , Int Ed Engl* , 1974, **13**, 539), no such comparison of dihedral angles can be made with the triepoxide of triphenylene

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