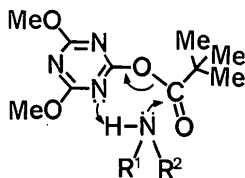


Fig. 2. The rate of aniline acylation by selected 'active' esters shown by decrease of substrate concentration with time (Kamiński, 1990).

enhanced reactivity of triazine esters may be the stabilization of the cyclic transition state (see below) in the acylation reaction by interaction of the nucleophilic agent with lone-pair electrons at a ring N (sp^2) atom (Kamiński, 1990) but there is no direct evidence for this.



The authors thank the Ministry of National Education and the Polish Academy of Sciences for

financial support under the projects RP.II.10 and CPBP 01.13.2.5.

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Acta Cryst. (1990). **C46**, 2214–2216

Structure of *syn*-1,2,3,4-Diepoxy-1,2,3,4-tetrahydronaphthalene

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(Received 27 December 1989; accepted 5 February 1990)

Abstract. *syn*-3,6-Dioxatetracyclo[6.4.0^{2,4}.0^{5,7}]dodeca-1(12),8,10-triene, C₁₀H₈O₂, $M_r = 160.2$, monoclinic,

$P2_1/n$, $a = 8.075$ (2), $b = 8.041$ (1), $c = 12.057$ (2) Å, $\beta = 107.59$ (1)°, $V = 746.2$ (4) Å³, $Z = 4$, $D_x = 1.426$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.93$ cm⁻¹, $F(000) = 336$, $T = 297$ K, $R = 0.032$ for 926 observations having $I > 2\sigma(I)$ (of 1313 unique

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Table 1. *Coordinates and equivalent isotropic thermal parameters*

	x	y	z	$B_{eq}(\text{\AA}^2)$
O1	0-6135 (1)	0-1164 (2)	0-75876 (9)	4-71 (3)
O2	0-6918 (1)	0-3093 (1)	0-95511 (9)	4-32 (3)
C1	0-7762 (2)	0-0258 (2)	0-7967 (1)	4-10 (4)
C2	0-6580 (2)	0-0292 (2)	0-8666 (1)	4-16 (4)
C3	0-7015 (2)	0-1335 (2)	0-9733 (1)	3-95 (3)
C4	0-8610 (2)	0-2315 (2)	1-0045 (1)	3-59 (3)
C5	0-9780 (2)	0-2240 (2)	0-9313 (1)	3-11 (3)
C6	1-1338 (2)	0-3110 (2)	0-9650 (1)	4-16 (4)
C7	1-2472 (2)	0-3015 (2)	0-9009 (2)	5-37 (4)
C8	1-2085 (2)	0-2044 (3)	0-8024 (2)	5-94 (5)
C9	1-0541 (2)	0-1158 (2)	0-7682 (1)	4-92 (4)
C10	0-9377 (2)	0-1244 (2)	0-8314 (1)	3-33 (3)

Table 2. *Bond angles ($^\circ$)*

C1—O1—C2	60-7 (1)	O2—C4—C5	117-6 (1)
C3—O2—C4	60-7 (1)	C3—C4—C5	119-9 (1)
O1—C1—C2	58-8 (1)	C4—C5—C6	119-5 (1)
O1—C1—C10	117-3 (1)	C4—C5—C10	120-9 (1)
C2—C1—C10	120-3 (1)	C6—C5—C10	119-6 (2)
O1—C2—C1	60-5 (1)	C5—C6—C7	120-6 (2)
O1—C2—C3	116-1 (1)	C6—C7—C8	120-2 (2)
C1—C2—C3	119-2 (1)	C7—C8—C9	119-9 (2)
O2—C3—C2	116-0 (1)	C8—C9—C10	120-8 (2)
O2—C3—C4	60-6 (1)	C1—C10—C5	120-5 (1)
C2—C3—C4	119-1 (1)	C1—C10—C9	120-6 (1)
O2—C4—C3	58-68 (9)	C5—C10—C9	118-9 (1)

data). The naphthalene ring system is slightly bowed, with deviation from coplanarity up to 0-036 (2) \AA . The epoxy groups are asymmetric, with the C—O bonds nearest the center of the molecule longer than those towards the outside.

Introduction. The title compound was prepared for the reinvestigation of naphthalene metabolism in rats (Tsang, Griffin, Horning & Stillwell, 1982; Griffin & Tsang, 1979). Since the *anti* and *syn* diepoxides have eluded detection as metabolites, the isolation and characterization of oxygenated and methylthio urinary metabolites of naphthalene have supported the presence of the *anti* isomer (Glusker, Carrell, Zacharias & Harvey, 1974; Neidle, Subbiah, Cooper & Riberio, 1980). Standard spectral studies (NMR, IR, MS) were conducted, but in order to ascertain the presence of any structural anomalies, the crystal structure determination of the *syn* isomer was conducted.

Experimental. Colorless crystals (EtOAc): m.p. 453 K [literature m.p. 451–453 K (Tsang *et al.*, 1982)], crystal dimensions 0-40 \times 0-28 \times 0-28 mm, Enraf-Nonius CAD-4 diffractometer with Mo $K\alpha$ radiation and graphite monochromator. Space group from systematic extinctions $h0l$ with $h+l$ odd, $0k0$ with k odd. Cell dimensions by least-squares fit of setting angles of 25 reflections with $15 < \theta < 16^\circ$. Intensity data by ω - 2θ scans, limits $9 \geq h \geq 0$, $9 \geq k$

≥ 0 , $13 \geq l \geq -13$, $1 \leq \theta \leq 25^\circ$. Max. scan time 180 s, scan rates 0-26–5-0 $^\circ \text{min}^{-1}$. Intensities of standard reflections 200, 020, 004 varied randomly; no decay correction. Data corrected for background, Lorentz, polarization; absorption negligible, 1313 unique data. $R_{\text{int}} = 0-010$ for redundant $0kl$ and $0k\bar{l}$ data, 926 observed data [$I > 2\sigma(I)$] used in refinement.

Structure solution by *MULTAN78* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Refinement by full-matrix least squares based on F with weights $w = 4F_o^2[\sigma^2(I) + (0-02F_o^2)^2]^{-1}$, non-H atoms anisotropic. H-atom positions located in difference maps, 0-40–0-49 $e \text{\AA}^{-3}$, and refined isotropically. Enraf-Nonius *SDP* programs used (Frenz & Okaya, 1980), scattering factors of Cromer & Waber (1974). Convergence achieved (maximum shift $< 0-01\sigma$) with $R = 0-064$ for all data, $wR = 0-048$, $S = 1-733$ for 142 variables, maximum residual $\pm 0-13 e \text{\AA}^{-3}$, extinction coefficient $g = 2-4 (4) \times 10^{-6}$, where the correction factor $(1 + gI_c)^{-1}$ was applied to F_c .

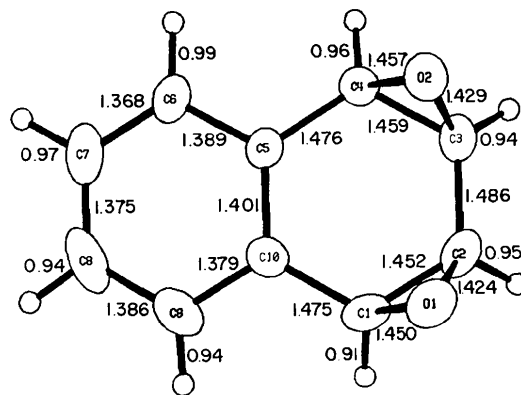


Fig. 1. Numbering scheme with bond distances [e.s.d.'s are 0-002 \AA (0-02 \AA for C—H)] for the title compound (ORTEP; Johnson, 1976).

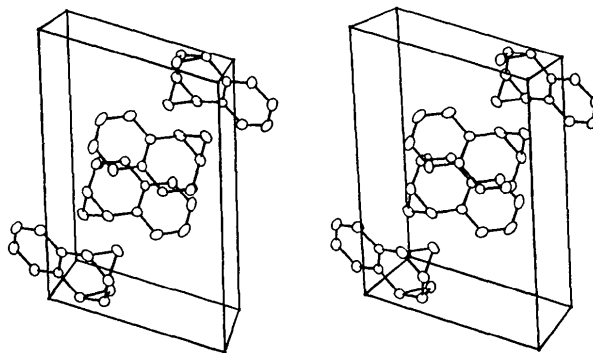


Fig. 2. Stereoview of the unit cell, viewed approximately down the b axis, with c vertical.

Discussion. Fractional coordinates are given in Table 1,* bond distances are in Fig. 1, bond angles are in Table 2, and the unit cell is shown in Fig. 2. The naphthalene ring system is nearly planar. It exhibits little structural distortion from the two fused three-membered rings, as all ten of its non-H atoms lie within 0.036 (2) Å of a common plane. The O atoms O1 and O2 lie 1.189 (1) and 1.184 (1) Å, respectively, out of this best plane. The deviation of the ring system from strict planarity consists of a bowing, such that the two six-membered rings, which are individually planar, form an angle of 2.6 (1)°, with the O atoms lying on the outside of the bow. The planes defined by the epoxy groups form angles with the best plane of the carbon ring system of 105.60 (6) and 106.34 (7)° for O1 and O2, respectively. The two planes of the epoxy groups intersect at an angle of 65.21 (11)°. The epoxy groups are asymmetric, with the C—O bonds nearest the center of the molecule [average 1.453 (2) Å], longer than

those toward the outside [average 1.427 (2) Å]. The angles at oxygen are both 60.7 (1)°. The geometry of the epoxy group is similar to that of *syn*-3,4-dimethoxy-1,2-epoxy-1,2,3,4-tetrahydronaphthalene (Klein & Stevens, 1984).

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* Lists of structure factors, anisotropic thermal parameters, isotropic thermal parameters, least-squares planes and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53029 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Acta Cryst. (1990). **C46**, 2216–2218

Structure of 9-Bromo-2,3-dihydro-8-methoxy-5,5-dimethyl-5H-benzo[b]pyrano-[3,4-b][1,4]dithiine

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(Received 4 November 1989; accepted 14 February 1990)

Abstract. C₁₄H₁₅BrO₂S₂, *M_r* = 359.31, monoclinic, *P*2₁/*c*, *a* = 8.607 (2), *b* = 16.120 (2), *c* = 12.597 (2) Å, β = 120.65 (1)°, *V* = 1503.5 (9) Å³, *Z* = 4, *D_x* =

1.59 Mg m⁻³, λ(Cu *K*α) = 1.54184 Å, μ = 6.28 mm⁻¹, *F*(000) = 728, *T* = 296 (1) K, *R* = 0.058, *wR* = 0.083 for 2385 unique observed reflections. The 1,3-biplanar pyran ring assumes an almost perfect skew conformation, whereas the dithiine ring exhibits a state transitional between ⁴*E* envelope and ⁴*S*₅ skew forms.

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