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3-(*o*-Carboxyphenyl)-1-ethyltriazene 1-Oxide†

Chitra Samanta,[a] Alok Kumar Mukherjee[a]* and Monika Mukherjee[b]

[a]*Department of Physics, Jadavpur University, Calcutta 700 032, India, and* [b]*Department of Solid State Physics, Indian Association for the Cultivation of Science, Calcutta 700 032, India. E-mail: akm@juphys.ernet.in*

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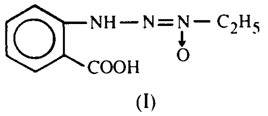
Abstract

The structure determination of the title compound, $C_9H_{11}N_3O_3$, establishes the *N*-oxide form of triazene. The two independent molecules in the asymmetric unit are hydrogen bonded and have different conformations. One molecule is essentially planar, while in the other molecule, the terminal ethyl and carboxy groups deviate considerably from the corresponding molecular plane. The planar phenyl ring and the trigonal-planar geometry about the triazene N atom bonded to the phenyl ring suggest a resonance interaction extending over adjacent atoms. Intermolecular hydrogen bonds link the molecules into infinite chains.

Comment

Substituted triazenes (*R*N═N—NH—) find wide-ranging applications as initiators of radical polymerization (Rapta *et al.*, 1996), as efficient chelating agents (Leman *et al.*, 1992; Cotton *et al.*, 1992) and as anti-tumor drugs (Wilman, 1988). As part of our systematic studies on the synthesis and characterization of triazene 1-oxide derivatives (Samanta *et al.*, 1985, 1997) and to build up a hierarchy for such systems, the structure determination of 3-(*o*-carboxyphenyl)-1-ethyltriazene 1-oxide, (I), was undertaken.



(I)

The results of the present X-ray analysis are in agreement with those of the structure analyses of similar substituted triazenes (Samanta *et al.*, 1997; Anulewicz, 1997; Neidle & Wilman, 1992) and establish the tautomeric *N*-oxide form of triazene (Smith *et al.*, 1992). The asymmetric unit of (I) (Fig. 1) consists of two independent molecules (*A* and *B*) which are approximately orthogonal to each other; the dihedral angle between the essentially planar molecule *A* (r.m.s. deviation 0.032 Å) and the planar part of molecule *B* through atoms C11–C17, N4–N6 and O6 (r.m.s. deviation 0.034 Å) is 85.11 (5)°. In molecule *B*, but not in *A*, the carboxy and ethyl groups are significantly out of the molecular plane (see torsion angles in Table 1). The N1 and N4 atoms, with bond angles summing to 360.0°, are sp^2 hybridized. Each displays trigonal-planar bonding geometry and coplanarity with the phenyl group, strongly suggesting a resonance interaction extending

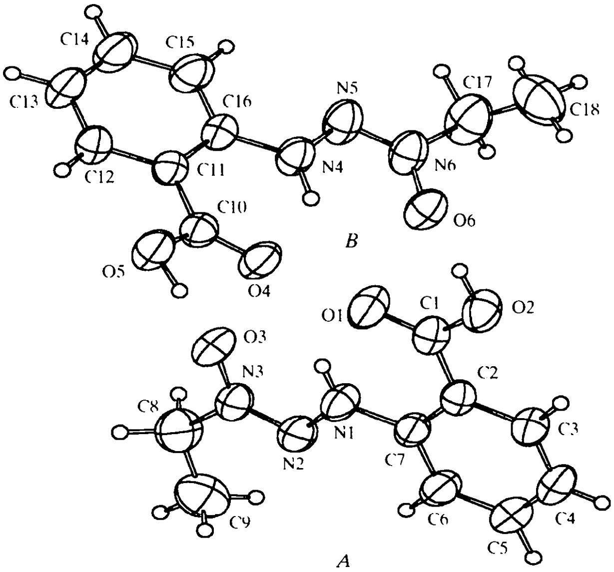


Fig. 1. View (50% probability level) of the two molecules in the asymmetric unit showing the atom-labelling scheme.

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† Alternative name: *o*-(3-ethyl-2-triazeno)benzoic acid N^3-oxide.

to the adjacent atoms. This is reflected in the shorter N1—C7 [1.393 (4) Å] and N4—C16 [1.383 (4) Å] bond lengths compared with N3—C8 [1.488 (4) Å] and N6—C17 [1.477 (5) Å]. The short N2—N3 and N5—N6 distances [1.264 (3) and 1.270 (4) Å, respectively] indicate double-bond character, and the N1—N2 and N4—N5 bonds [1.332 (4) and 1.327 (4) Å] are shorter than pure single bonds.

N—H···O, C—H···N and C—H···O interactions (Table 2) influence the conformations of molecules *A* and *B*, and the crystal packing. Three of the resulting four pseudo-rings in molecules *A* and *B* are fused with the benzene rings. The crystal packing is stabilized by intra- and intermolecular hydrogen bonds *via* carboxy O atoms. The molecules are linked by O—H···O hydrogen bonds into infinite chains with the sequence *A*···*B*···*A*···*B*.

Experimental

The title compound was prepared according to the procedure of Samanta *et al.* (1997). Single crystals were obtained by slow evaporation from an ethanol solution.

Crystal data

$C_9H_{11}N_3O_3$
$M_r = 209.21$
Orthorhombic
Pbca
$a = 19.862\ (1)$ Å
$b = 21.301\ (1)$ Å
$c = 9.758\ (1)$ Å
$V = 4128.4\ (5)$ Å^3
$Z = 16$
$D_x = 1.346$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 23$–$30°$
$\mu = 0.871$ mm^{-1}
$T = 293\ (2)$ K
Prism
$0.35 \times 0.25 \times 0.10$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.611$, $T_{\max} = 0.895$
2505 measured reflections
2505 independent reflections

1710 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 60.07°$
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 23$
$l = 0 \rightarrow 10$
3 standard reflections every 150 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.121$
$S = 1.06$
2505 reflections
271 parameters
H atoms fixed
$w = 1/[\sigma^2(F_o^2) + (0.071P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.179$ e Å^{-3}
$\Delta\rho_{\min} = -0.181$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.217 (4)	O4—C10	1.222 (3)
O2—C1	1.325 (4)	O5—C10	1.317 (4)
O3—N3	1.288 (3)	O6—N6	1.294 (3)
N1—N2	1.332 (4)	N4—N5	1.327 (4)
N1—C7	1.393 (4)	N4—C16	1.383 (4)
N2—N3	1.264 (3)	N5—N6	1.270 (4)
N3—C8	1.488 (4)	N6—C17	1.477 (5)
C1—C2	1.477 (5)	C10—C11	1.472 (4)
C8—C9	1.490 (6)	C17—C18	1.472 (6)
N2—N1—C7	119.1 (3)	N5—N4—C16	120.1 (3)
N3—N2—N1	111.4 (3)	N6—N5—N4	111.6 (3)
N2—N3—O3	123.9 (3)	N5—N6—O6	123.2 (3)
N2—N3—C8	118.4 (3)	N5—N6—C17	117.8 (3)
O3—N3—C8	117.6 (3)	O6—N6—C17	118.9 (3)
O1—C1—O2	121.5 (3)	O4—C10—O5	121.4 (3)
O1—C1—C2	124.6 (3)	O4—C10—C11	124.9 (3)
O2—C1—C2	113.8 (3)	O5—C10—C11	113.7 (3)
N3—C8—C9	115.5 (3)	C18—C17—N6	110.7 (4)
C7—N1—N2—N3	−178.6 (3)	C16—N4—N5—N6	−177.6 (3)
N1—N2—N3—C8	−179.7 (3)	N4—N5—N6—C17	−177.8 (3)
O2—C1—C2—C3	2.3 (5)	O5—C10—C11—C12	−13.5 (5)
O1—C1—C2—C7	0.3 (5)	O4—C10—C11—C16	−12.1 (5)
N2—N3—C8—C9	3.6 (5)	N5—N6—C17—C18	113.9 (4)
O3—N3—C8—C9	−175.6 (3)	O6—N6—C17—C18	−62.8 (5)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	2.653 (4)	131.6
N1—H1···O3	2.475 (3)	104.5
C3—H3···O2	2.713 (4)	101.2
C6—H6···N2	2.753 (4)	99.5
N4—H4*A*···O4	2.641 (4)	133.2
N4—H4*A*···O6	2.473 (3)	105.3
C12—H12···O5	2.722 (4)	99.6
C15—H15···N5	2.777 (4)	98.7
O5—H5*A*···O3	2.608 (3)	167.7
O2—H2···O6^{i}	2.657 (3)	170.9

Symmetry code: (i) $x, y, z - 1$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *MULTAN*88 (Debaerdemaeker *et al.*, 1988). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1995; Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1213). Services for accessing these data are described at the back of the journal.

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A Sultone Derived from Racemic Camphene

Kenneth W. Muir,[a] Colin S. Rodger,[a] David G. Morris[a] and Karl S. Ryder[b]

[a]*Chemistry Department, University of Glasgow, Glasgow G12 8QQ, Scotland, and* [b]*Chemistry Department, University of Aberdeen, Aberdeen AB24 3UE, Scotland. E-mail: k.muir@chem.gla.ac.uk*

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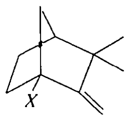
Abstract

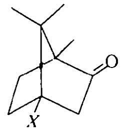
A controversy about the structures of five-membered ring sultones obtained by treatment of camphenes with acetic and concentrated sulfuric acids has been resolved by X-ray analysis of the sultone obtained from racemic camphene, namely, *endo*-3*H*-10,10-dimethyl-4-oxa-5-thiatricyclo[5.2.1.$0^{3,7}$]decane *S*,*S*-dioxide, (also known as 10-bornanesulfonic acid 2-hydroxy-γ-sultone), $C_{10}H_{16}O_3S$. Five-membered saturated sultone rings are shown to be conformationally flexible.

Comment

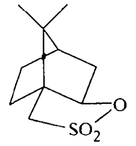
1-Substituted camphenes, (1), are convenient starting materials for the synthesis of 4-substituted camphors, (2) (Berson, 1963). However, this transformation, which involves treatment of (1) with acetic acid dissolved in concentrated sulfuric acid, on occasion gives rise to such large quantities of sultone by-product as to require the development of an alternative synthetic route (Morris & Murray, 1975). The sultone arising from unsubstituted camphene, (1*a*), was assigned structure (3) by Lipp & Holl (1929). Subsequently, a systematic investigation of the reaction led to the revised structure, (4); the configuration at the C atoms common to the sultone and norbornane residues was not specified, and could be either both *exo*, as shown, or both *endo* (Asahina & Kawahata, 1939; Asahina *et al.*, 1938).



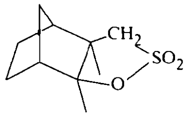
(1*a*) X = H
(1*b*) X = NO_2
(1*c*) X = CO_2H



(2)



(3)



(4)

We have, therefore, subjected the sultone formed from camphene, (1*a*), to single-crystal X-ray analysis. Racemic (1*a*) was used as the starting material because a racemization step, which is not always complete, is almost certainly involved in the formation of the sultone. The molecule (Fig. 1) has structure (3), as proposed by Lipp & Holl (1929). It seems likely that substituted camphenes, such as (1*b*) or (1*c*), also give rise to sultones like (3), rather than (4), and that the suggestions of Asahina (Asahina & Kawahata, 1939; Asahina *et al.*, 1938) should be disregarded.

Bond lengths in (3) (Table 1) show deviations of up to 0.03 Å from standard values. Thus, the staggered conformation across C1—C7 [1.556 (2) Å] leads to a

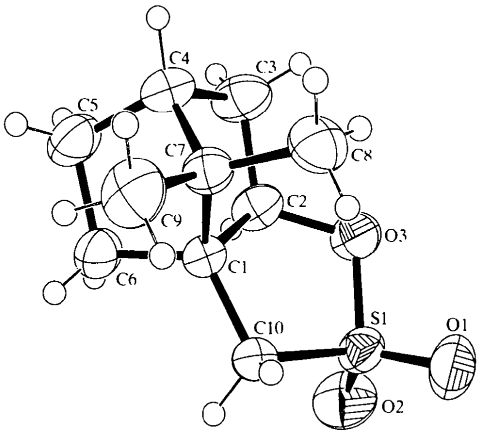


Fig. 1. A view of the title sultone molecule, (3), showing 50% probability ellipsoids. H atoms are shown as spheres of arbitrary radii.