Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1211). Services for accessing these data are described at the back of the journal.

References

Enraf–Nonius (1994). *CAD-4 Express*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Metz, P. & Hungerhoff, B. (1996). *GIT Fachz. Lab.* **40**, 690–691.
Metz, P. & Hungerhoff, B. (1997). *J. Org. Chem.* **62**, 4442–4448.
Metz, P. & Linz, C. (1994). *Tetrahedron*, **50**, 3951–3966, and references therein.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1990). *XP. Interactive Molecular Graphics Program*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1997). C**53**, 1657–1658

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

Chitra Samanta,[a] Sailesh C. Saha[b] and Alok Kumar Mukherjee[a]

[a]*Department of Physics, Jadavpur University, Calcutta 700 032, India, and* [b]*Department of Chemistry, Jadavpur University, Calcutta 700 032, India. E-mail: sspmm@iacs.ernet.in*

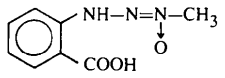
(*Received 27 March 1997; accepted 29 April 1997*)

Abstract

The structure determination of the title compound, $C_8H_9N_3O_3$, establishes the *N*-oxide form of triazene. The overall molecular planarity and trigonal planar geometry of the triazene N atom bonded to the phenyl ring suggest a resonance interaction extending over adjacent atoms. The molecular conformation is stabilized by intramolecular hydrogen bonds and the crystal packing by intermolecular hydrogen bonds.

Comment

Substituted triazenes increasingly find applications as initiators of radical polymerization (Rapta *et al.*, 1996), as efficient chelating agents (Saha, Chakraborty, Roychaudhuri & Maji, 1992) and as antitumor drugs (Wilman, 1988). As part of our studies on the synthesis and characterization of triazene 1-oxide derivatives and to build up a hierarchy for such systems, the structure determination of 3-(*o*-carboxyphenyl)-1-methyltriazene 1-oxide, (I), was undertaken.



(I)

The results of the present X-ray analysis are in agreement with those of analyses of corresponding substituted phenyltriazene 1-oxide structures (Sarkar, Khalil, Saha & Talapatra, 1983; Samanta, De, Sarkar, Saha & Talapatra, 1985) and establish the tautomeric *N*-oxide form of triazene (Smith *et al.*, 1992). Torsion angles close to 0 and 180°, and the r.m.s deviation of 0.051 Å from the least-squares plane through the non-H atoms illustrate the overall molecular planarity. The essentially planar phenyl moiety and trigonal-planar geometry of the triazene N1 atom strongly suggest a resonance interaction extending over the C6, N1, N2 and N3 atoms. The short N2—N3 distance [1.263 (2) Å] indicates double-bond character and the N1—N2 distance [1.323 (2) Å] is shorter than a pure single bond. The deviation of O3 [0.122 (1) Å] from the molecular plane causes conjugation between N3 and C8 to be less effective and is reflected in the longer N3—C8 bond length [1.459 (2) Å] compared with the N1—C6 distance [1.390 (2) Å].

The almost planar conformation of the molecule is a result of intramolecular hydrogen bonding; there are two N—H···O interactions and two C—H···O interactions (see Table 2). Three of the resulting four pseudo-rings

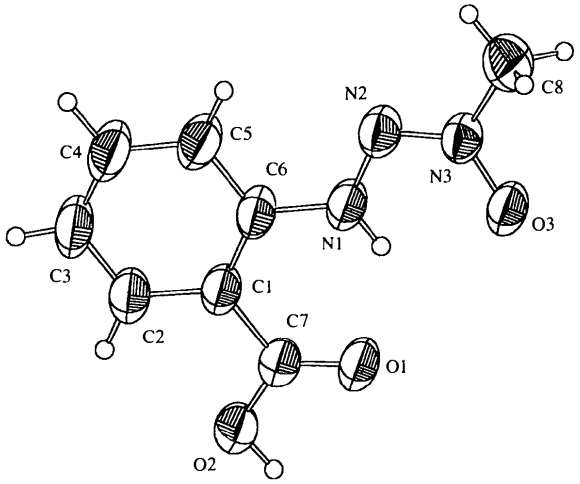


Fig. 1. *ORTEP*II (Johnson, 1976; Zsolnai, 1995) view (50% probability level) of the molecule showing the atom-labelling scheme.

---

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

are fused with the benzene ring. The crystal packing is stabilized by intermolecular hydrogen bonds. The molecules are joined *via* O2···O3, forming infinite hydrogen-bonded chains.

Experimental

The title compound was prepared according to the procedure of Majumdar, Bhattacharyya & Ray (1971). Suitable single crystals were obtained by slow evaporation from ethanol solution.

Crystal data

$C_8H_9N_3O_3$
$M_r = 195.18$
Monoclinic
$P2_1/c$
$a = 6.681$ (3) Å
$b = 8.362$ (1) Å
$c = 16.707$ (2) Å
$\beta = 97.01$ (5)°
$V = 926.4$ (4) Å^3
$Z = 4$
$D_x = 1.399$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8$–16°
$\mu = 0.110$ mm^{-1}
$T = 293$ (2) K
Prism
0.5 × 0.4 × 0.3 mm
White

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
1527 measured reflections
1401 independent reflections
1158 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.010$
$\theta_{\rm max} = 24.95°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 9$
$l = -19 \rightarrow 19$
3 standard reflections every 100 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.109$
$S = 1.123$
1401 reflections
163 parameters
H-atom positions refined with isotropic U

$w = 1/[\sigma^2(F_o^2) + (0.0875P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.066$
$\Delta\rho_{\rm max} = 0.166$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.193$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C7	1.210 (2)	C1—C6	1.391 (2)
O2—C7	1.324 (2)	C1—C2	1.394 (2)
O3—N3	1.288 (2)	C1—C7	1.477 (2)
N1—N2	1.323 (2)	C2—C3	1.373 (3)
N1—C6	1.390 (2)	C3—C4	1.361 (3)
N2—N3	1.263 (2)	C4—C5	1.374 (2)
N3—C8	1.459 (2)	C5—C6	1.399 (2)
N2—N1—C6	120.30 (15)	C2—C1—C7	120.30 (15)
N3—N2—N1	112.28 (14)	N1—C6—C1	120.13 (14)
N2—N3—O3	123.03 (13)	C1—C6—C5	119.93 (15)
N2—N3—C8	118.24 (15)	O1—C7—O2	121.56 (15)
O3—N3—C8	118.71 (14)	O1—C7—C1	124.86 (14)
C6—C1—C7	121.42 (13)	O2—C7—C1	113.58 (13)
C2—C1—C7—O2	1.8 (2)	C7—C1—C6—C5	177.2 (2)
C6—C1—C7—O2	−177.47 (15)	N2—N1—C6—C1	−179.80 (14)
C2—C1—C7—O1	−177.6 (2)	C6—N1—N2—N3	175.06 (13)
C6—C1—C7—O1	3.1 (3)	N1—N2—N3—O3	0.8 (2)
C7—C1—C6—N1	−2.8 (2)	N1—N2—N3—C8	179.2 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H6···O3	0.82 (2)	2.10 (2)	2.471 (2)	108 (2)
N1—H6···O1	0.82 (2)	2.03 (2)	2.645 (2)	131 (2)
C2—H1···O2	0.95 (2)	2.38 (2)	2.710 (2)	100 (1)
C5—H4···N2	0.96 (2)	2.44 (2)	2.756 (3)	99 (1)
O2—H5···O3$^{\rm i}$	0.90 (3)	1.76 (3)	2.643 (2)	165 (2)
C8—H7···O3$^{\rm ii}$	0.91 (3)	2.40 (3)	3.299 (3)	168 (2)

Symmetry codes: (i) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $2 - x, \frac{1}{2} + y, \frac{3}{2} - z$.

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) and *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Software used to prepare material for publication: *SHELXL*93.

The authors wish to thank Professor S. Sarkar, Department of Chemistry, Indian Institute of Technology, Kanpur, India, for providing the X-ray diffractometer data.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1193). Services for accessing these data are described at the back of the journal.

References

Debaerdemaeker, T., Germain, G., Main, P., Refaat, L. S., Tate, C. & Woolfson, M. (1988). *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Universities of York, England, and Louvain, Belgium.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Majumdar, A. K., Bhattacharyya, B. C. & Ray, B. C. (1971). *Anal. Chim. Acta*, **57**, 425–428.

Rapta, P., Omelka, L., Stasko, A., Dauth, J., Deubzer, B. & Weis, J. (1996). *J. Chem. Soc. Perkin Trans.* 2, pp. 255–261.

Saha, S. C., Chakraborty, P. K., Roychaudhuri, N. & Maji, S. (1992). *Indian J. Chem.* **31**A, 260–264.

Samanta, C., De, P. K., Sarkar, S. B., Saha, S. C. & Talapatra, S. K. (1985). *Acta Cryst.* **C41**, 142–144.

Sarkar, S. B., Khalil, Md., Saha, S. C. & Talapatra, S. K. (1983). *Acta Cryst.* **C39**, 1075–1076.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Smith, R. H. Jr, Wladkowski, B. D., Herling, J. A., Pfaltzgraff, T. D., Pruski, B., Klose, J. & Michejda, Ch. J. (1992). *J. Org. Chem.* **57**, 654–661.

Wilman, D. E. V. (1988). *Cancer Treat. Rev.* **15**, 69–72.

Zsolnai, L. (1995). *ZORTEP. An Interactive ORTEP Program*. University of Heidelberg, Germany.