GOLDBERG, I. (1980). *The Chemistry of Functional Groups. Supplement E: The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and their Sulphur Analogues.* Part 1, edited by S. PATAI, pp. 175–214. Chichester: John Wiley.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

NAGANO, O., KOBAYASHI, A. & SASAKI, I. (1978). *Bull. Chem. Soc. Jpn*, **51**, 790–793.

SHELDRICK, G. M. (1983). *SHELXTL*, revision 4·0, January 1983. *An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen.

TRUEBLOOD, K. N., KNOBLER, C. B., LAWRENCE, D. S. & STEVENS, R. V. (1982). *J. Am. Chem. Soc.* **104**, 1355–1362.

VÖGTLE, F., SIEGER, H. & MÜLLER, W. M. (1981). *Topics in Current Chemistry* 98. *Host Guest Complex* I, edited by F. VÖGTLE, pp. 107–161. Berlin: Springer-Verlag.

WIPFF, G., KOLLMAN, P. A. & LEHN, J. M. (1983). *J. Mol. Struct.* **93**, 153–165.

WIPFF, G., WEINER, P. & KOLLMAN, P. (1982). *J. Am. Chem. Soc.* **105**, 3249–3258.

Acta Cryst. (1985). C**41**, 140–142

The Structure of Dispiro(tricyclo[3.3.1.1^{3,7}]decane-2,6′-6′*H*,12′*H*-dibenzo[*b*,*f*][1,5]dioxocin-12′,2′′-tricyclo[3.3.1.1^{3,7}]decane), $C_{32}H_{36}O_2$

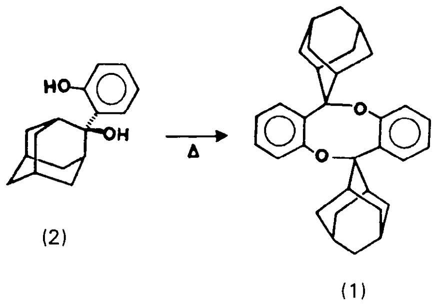
BY MARY F. GARBAUSKAS, IRENE A. EVANS AND JOHN J. TALLEY

General Electric Corporate Research and Development, PO Box 8, *Schenectady, NY* 12301, *USA*

(*Received* 30 *May* 1984; *accepted* 18 *September* 1984)

Abstract. $M_r = 456{\cdot}7$, monoclinic, $P2_1/a$, $a = 13{\cdot}961\,(8)$, $b = 11{\cdot}189\,(6)$, $c = 16{\cdot}208\,(9)$ Å, $\beta = 107{\cdot}94\,(4)°$, $V = 2408{\cdot}7$ Å^3, $Z = 4$, $D_x = 1{\cdot}26$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71079$ Å, $\mu = 0{\cdot}8$ cm^{-1}, $F(000) = 495{\cdot}94$, approximately 303 K, $R = 0{\cdot}0635$, 1901 unique observed reflections. The central 1,5-dioxocin ring adopts a tub shape to minimize non-bonded interactions between the two very bulky adamantane moieties. This conformation leads to bridgehead carbons that are shift inequivalent in the proton-decoupled ^{13}C NMR spectrum and explains the presence of the nine aliphatic NMR resonances observed for this molecule.

Introduction. A sample of (1) was prepared by the thermolysis of (2) (Talley & Evans, 1984) in the melt at 443 K. As (2) melted, 437 K, it acquired an orange color; continued heating resulted in the evolution of water vapor and the resolidification of (1) as a white solid with m.p. 500–501 K.



(2)

(1)

The solution ^{13}C NMR of (1) contained four resonances in the aromatic region and nine resonances in the aliphatic region. Since the ^{13}C NMR of (2) showed only seven aliphatic resonances in addition to four aromatic signals, the formation of an unusual structure or conformation was suspected. The field desorption mass spectrum of (1) confirmed that a dimer with a molecular formula of $C_{32}H_{36}O_2$ had been formed.

In order to establish unequivocally the structure of the dimer, we performed a single-crystal X-ray analysis of (1).

Experimental. Rectangular thin plates obtained by crystallization from acetone. Data collected on Nicolet P3/F automated diffractometer, monochromated Mo $K\alpha$ radiation, crystal dimensions $0{\cdot}2 \times 0{\cdot}3 \times 0{\cdot}05$ mm. Lattice parameters from 12 reflections with 5 to 14° 2θ. $h = 0$ to 15, $k = 0$ to 12, $l = -16$ to 16, max. $\sin\theta/\lambda = 0{\cdot}54$ Å^{-1}. Two standard reflections, $00\bar{3}$ and $\bar{1}1\bar{2}$, monitored with s.d. in intensity of 1% in both cases. 3524 reflections collected; 1901 unique observed with $F \geq 3\sigma(F)$. Structure solved by direct methods using *SHELXTL* (Sheldrick, 1981). Refinement based on F. Hydrogen positions located by difference Fourier synthesis. In final stages of refinement, C—H bond lengths and H—C—H angles fixed at 0·96 Å and 109·5°. Fixed isotropic temperature factor of 0·06 Å^2 for all H atoms. All non-hydrogen atoms anisotropic. 307 parameters refined, final $R_w = 0{\cdot}0488$, $R = 0{\cdot}0635$. $w^{-1} = \sigma^2(F) + (0{\cdot}00026)F^2$. In final difference Fourier map, max. and min. 0·24 and $-0{\cdot}25$ e Å^{-3}. Max.

0108-2701/85/010140-03$01.50

Table 1. *Atom coordinates* ($\times 10^4$) *and temperature factors* ($Å^2 \times 10^3$)

	x	y	z	U_{eq}*
O(1)	−429 (2)	6129 (2)	2193 (2)	38 (1)
O(2)	1560 (2)	6319 (2)	3261 (2)	38 (1)
C(1)	−139 (3)	7081 (3)	1782 (2)	34 (2)
C(2)	649 (3)	7827 (3)	2251 (2)	35 (2)
C(3)	934 (3)	8733 (4)	1782 (3)	49 (2)
C(4)	441 (4)	8915 (4)	908 (3)	60 (2)
C(5)	−365 (4)	8212 (4)	482 (3)	54 (2)
C(6)	−655 (3)	7290 (4)	914 (3)	45 (2)
C(7)	1011 (3)	5150 (3)	1954 (2)	35 (2)
C(8)	1756 (3)	5846 (3)	2536 (2)	36 (2)
C(9)	2667 (3)	6065 (4)	2411 (3)	47 (2)
C(10)	2863 (3)	5640 (4)	1682 (3)	51 (2)
C(11)	2138 (3)	5009 (4)	1077 (3)	49 (2)
C(12)	1224 (3)	4773 (4)	1207 (3)	44 (2)
C(13)	8 (3)	4938 (3)	2116 (2)	37 (2)
C(14)	92 (3)	4314 (4)	2987 (3)	44 (2)
C(15)	399 (4)	3001 (4)	2946 (3)	60 (2)
C(16)	−408 (4)	2333 (4)	2245 (3)	69 (2)
C(17)	−1421 (4)	2401 (4)	2421 (3)	81 (3)
C(18)	−1718 (4)	3710 (4)	2432 (3)	63 (2)
C(19)	−929 (3)	4361 (4)	3150 (3)	55 (2)
C(20)	−775 (3)	4241 (4)	1393 (3)	45 (2)
C(21)	−491 (3)	2910 (4)	1377 (3)	60 (2)
C(22)	−1803 (3)	4283 (4)	1554 (3)	57 (2)
C(23)	1208 (3)	7576 (3)	3205 (2)	34 (2)
C(24)	517 (3)	7631 (3)	3787 (2)	38 (2)
C(25)	217 (3)	8927 (3)	3889 (3)	45 (2)
C(26)	1140 (3)	9670 (4)	4344 (3)	47 (2)
C(27)	1702 (3)	9156 (4)	5237 (3)	58 (2)
C(28)	2023 (3)	7871 (4)	5116 (3)	53 (2)
C(29)	1078 (3)	7129 (4)	4690 (3)	51 (2)
C(30)	2131 (3)	8371 (3)	3632 (3)	41 (2)
C(31)	2694 (3)	7864 (4)	4530 (3)	52 (2)
C(32)	1823 (3)	9668 (4)	3767 (3)	48 (2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

$\Delta/\sigma = 0{\cdot}0$. Scattering factors and f', f'' supplied by computer programs.

Discussion. Final atomic coordinates for all non-hydrogen atoms are presented in Table 1, with derived bond lengths and angles presented in Table 2. A thermal-ellipsoid (50%) drawing containing the numbering scheme employed is shown in Fig. 1.*

The presence of nine aliphatic resonances in the proton-decoupled ^{13}C NMR spectrum of (1) is consistent with the structural data. The central 1,5-dioxocin ring adopts a tub shape to minimize non-bonded interactions between the two very bulky adamantane moieties. While the two bridgehead carbons adjacent to the alcohol moiety in (2) are shift equivalent, the bridgehead carbons adjacent to the oxygen in (1) are in different environments. One of the bridgehead carbons is below the tub and one is above it. The chemical shift of each carbon within one adamantane is unique, and has an identical partner in the second adamantane ring.

The typical dehydration product of an *o*-hydroxybenzyl alcohol derivative bearing a β hydrogen

Table 2. *Bond lengths* (Å) *and angles* (°)

O(1)–C(1)	1·380 (5)	O(1)–C(13)	1·487 (5)
O(2)–C(8)	1·389 (5)	O(2)–C(23)	1·484 (4)
C(1)–C(2)	1·404 (5)	C(1)–C(6)	1·389 (5)
C(2)–C(3)	1·396 (6)	C(2)–C(23)	1·529 (5)
C(3)–C(4)	1·386 (6)	C(4)–C(5)	1·372 (6)
C(5)–C(6)	1·375 (7)	C(7)–C(8)	1·405 (5)
C(7)–C(12)	1·398 (6)	C(7)–C(13)	1·520 (6)
C(8)–C(9)	1·371 (6)	C(9)–C(10)	1·378 (7)
C(10)–C(11)	1·369 (5)	C(11)–C(12)	1·381 (6)
C(13)–C(14)	1·546 (6)	C(13)–C(20)	1·546 (5)
C(14)–C(15)	1·538 (6)	C(14)–C(19)	1·529 (7)
C(15)–C(16)	1·526 (6)	C(16)–C(17)	1·529 (8)
C(16)–C(21)	1·520 (7)	C(17)–C(18)	1·523 (6)
C(18)–C(19)	1·519 (6)	C(18)–C(22)	1·533 (7)
C(20)–C(21)	1·543 (6)	C(20)–C(22)	1·536 (6)
C(23)–C(24)	1·543 (6)	C(23)–C(30)	1·544 (5)
C(24)–C(25)	1·532 (5)	C(24)–C(29)	1·538 (5)
C(25)–C(26)	1·520 (5)	C(26)–C(27)	1·530 (5)
C(26)–C(32)	1·528 (7)	C(27)–C(28)	1·535 (6)
C(28)–C(29)	1·532 (6)	C(28)–C(31)	1·526 (7)
C(30)–C(31)	1·534 (5)	C(30)–C(32)	1·549 (6)

C(1)–O(1)–C(13)	117·5 (3)	C(8)–O(2)–C(23)	117·2 (3)
O(1)–C(1)–C(2)	119·7 (3)	O(1)–C(1)–C(6)	118·8 (3)
C(2)–C(1)–C(6)	121·5 (4)	C(1)–C(2)–C(3)	116·5 (3)
C(1)–C(2)–C(23)	120·5 (3)	C(3)–C(2)–C(23)	122·8 (3)
C(2)–C(3)–C(4)	121·8 (4)	C(3)–C(4)–C(5)	120·2 (5)
C(4)–C(5)–C(6)	119·9 (4)	C(1)–C(6)–C(5)	120·0 (4)
C(8)–C(7)–C(12)	116·0 (4)	C(8)–C(7)–C(13)	120·1 (4)
C(12)–C(7)–C(13)	123·7 (3)	O(2)–C(8)–C(7)	118·7 (4)
O(2)–C(8)–C(9)	119·4 (3)	C(7)–C(8)–C(9)	121·9 (4)
C(8)–C(9)–C(10)	120·3 (3)	C(9)–C(10)–C(11)	119·6 (4)
C(10)–C(11)–C(12)	120·2 (4)	C(7)–C(12)–C(11)	121·9 (3)
O(1)–C(13)–C(7)	107·3 (3)	O(1)–C(13)–C(14)	104·2 (3)
C(7)–C(13)–C(14)	114·4 (3)	O(1)–C(13)–C(20)	107·7 (3)
C(7)–C(13)–C(20)	114·9 (3)	C(14)–C(13)–C(20)	107·6 (3)
C(13)–C(14)–C(15)	109·6 (4)	C(13)–C(14)–C(19)	109·2 (3)
C(15)–C(14)–C(19)	109·1 (4)	C(14)–C(15)–C(16)	110·4 (3)
C(15)–C(16)–C(17)	110·4 (4)	C(15)–C(16)–C(21)	108·0 (4)
C(17)–C(16)–C(21)	109·9 (4)	C(16)–C(17)–C(18)	108·7 (4)
C(17)–C(18)–C(19)	109·5 (3)	C(17)–C(18)–C(22)	109·5 (4)
C(19)–C(18)–C(22)	110·0 (4)	C(14)–C(19)–C(18)	110·2 (4)
C(13)–C(20)–C(21)	112·0 (3)	C(13)–C(20)–C(22)	109·6 (4)
C(21)–C(20)–C(22)	106·9 (4)	C(16)–C(21)–C(20)	110·0 (4)
C(18)–C(22)–C(20)	109·6 (3)	O(2)–C(23)–C(2)	107·0 (3)
O(2)–C(23)–C(24)	105·0 (3)	C(2)–C(23)–C(24)	113·0 (3)
O(2)–C(23)–C(30)	107·7 (3)	C(2)–C(23)–C(30)	116·3 (3)
C(24)–C(23)–C(30)	107·2 (3)	C(23)–C(24)–C(25)	110·3 (3)
C(23)–C(24)–C(29)	109·7 (3)	C(25)–C(24)–C(29)	108·6 (3)
C(24)–C(25)–C(26)	110·5 (3)	C(25)–C(26)–C(27)	111·3 (3)
C(25)–C(26)–C(32)	107·3 (3)	C(27)–C(26)–C(32)	110·1 (3)
C(26)–C(27)–C(28)	108·4 (3)	C(27)–C(28)–C(29)	108·7 (3)
C(27)–C(28)–C(31)	110·1 (4)	C(29)–C(28)–C(31)	109·0 (3)
C(24)–C(29)–C(28)	110·2 (3)	C(23)–C(30)–C(31)	109·0 (3)
C(23)–C(30)–C(32)	111·9 (3)	C(31)–C(30)–C(32)	107·2 (3)
C(28)–C(31)–C(30)	110·8 (3)	C(26)–C(32)–C(30)	109·9 (3)

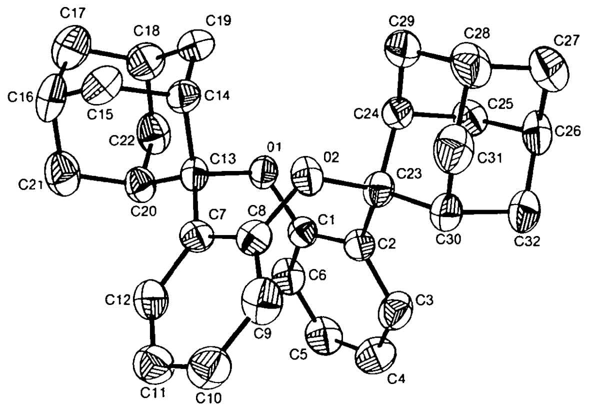


Fig. 1. Thermal-ellipsoid (50%) drawing containing the numbering scheme employed. Hydrogens have been omitted for clarity.

---

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39761 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

is the corresponding *o*-hydroxystyrene. Since the product of this type of dehydration would have been a very strained bridgehead olefin, the unusual dehydration product (1) was formed.

References

Sheldrick, G. M. (1981). Nicolet *SHELXTL* Operations Manual, revision 3. Nicolet XRD Corporation, Madison, WI, USA.

Talley, J. J. & Evans, I. A. (1984). *J. Org. Chem.* Submitted.

Acta Cryst. (1985). C**41**, 142–144

Structure of 3-(*o*-Hydroxyphenyl)-1-phenyltriazene 1-Oxide, $C_{12}H_{11}N_3O_2$

By Chitra Samanta, P. K. De, S. B. Sarkar, S. C. Saha[*] and S. K. Talapatra[†]

X-ray Laboratory, Department of Physics, Jadavpur University, Calcutta–700032, *India*

(*Received* 9 *March* 1984; *accepted* 19 *September* 1984)

Abstract. $M_r = 229{\cdot}0$, monoclinic, $P2_1/n$, $a = 6{\cdot}569\ (2)$, $b = 11{\cdot}870\ (4)$, $c = 13{\cdot}889\ (4)$ Å, $\beta = 94{\cdot}95\ (2)^\circ$, $V = 1078{\cdot}9\ (6)$ Å^3, $Z = 4$, $D_m = 1{\cdot}38$ (flotation in aq. KI), $D_x = 1{\cdot}41$ Mg m^{-3}, Mo $K\alpha$, $\bar{\lambda} = 0{\cdot}71073$ Å, $\mu = 1{\cdot}06$ mm^{-1}, $F(000) = 480$, room temperature, final $R = 0{\cdot}040$ for 1449 independent reflections. The structure establishes the *N*-oxide form of triazene and reveals both intramolecular N—H···O = 2·476 (2) Å and intermolecular O—H···O = 2·738 (3) Å hydrogen bonds. The molecules are nearly planar, with the phenyl ring on N(1) further out of the plane than that on N(3). The C—N bond lengths are not equal.

Introduction. The hydroxyphenyl or alkylphenyl triazenes, used as potential analytical reagents (Purohit, 1967; Chakraborti & Majumdar, 1977) and complexing agents (Datta & Sharma, 1983), have been shown from IR spectra to exist predominantly in the tautomeric *N*-oxide form (Mitsuhashi, Osamura & Simamura, 1965; Chakraborty, Behera & Zacharias, 1968) with the consequent presence of a $>$NH group. But the NH stretch appears displaced to comparatively much lower energies, one at 3240–3280 cm^{-1} and another at 3200 cm^{-1}, the displacements being caused in the former by intra- and the latter by intermolecular hydrogen bonds. The latter band is found to be absent when CH_3, Cl and OCH_3 groups are present in *ortho* positions of the phenyl ring, possibly because steric hindrance prevents formation of intermolecular hydrogen bonds (Behera & Zacharias, 1971). In order to confirm the *N*-oxide form and the nature of the hydrogen bonding, it was considered worthwhile to investigate the structure of such triazenes having *ortho* substitutions. In our first communication (Sarkar, Khalil, Saha & Talapatra, 1983) we reported the structure of 3-(*o*-carboxyphenyl)-1-phenyltriazene 1-oxide in which the *N*-oxide structure and both types of hydrogen bonds were found. The present study reports the structure of 3-(*o*-hydroxyphenyl)-1-phenyltriazene 1-oxide, which was prepared by coupling diazotized *o*-aminophenol with phenylhydroxylamine.

Experimental. Deep-brown crystal (from ethanol), 0·35 × 0·22 × 0·20 mm; Enraf–Nonius CAD-4 computer-controlled four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation; $h = 0$–±7, $k = 0$–13, $l = 0$–16; least-squares cell parameters from 25 carefully selected reflections from all octants in reciprocal space. Scattering factors for non-hydrogen atoms from *International Tables for X-ray Crystallography* (1962), for H atoms from Stewart, Davidson & Simpson (1965). 1997 $\pm hkl$ with $2\theta < 50^\circ$, 1449 independent, 548 with $I < 2\sigma(I)$ of which 178 have zero intensity, Lp correction, absorption ignored, $R_{\rm int} = 0{\cdot}078$. Structure solved by direct methods (*MULTAN*78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and Fourier technique. Non-hydrogen atoms anisotropic full matrix, H atoms [both H(5) and H(6) from ΔF synthesis, others, associated with benzene ring, calculated from trigonal geometry around C atoms] isotropic. Max. and min. heights in final difference Fourier map $\pm0{\cdot}2$ e Å^{-3}, max. Δ/σ 0·485, av. Δ/σ 0·065, final $R = 0{\cdot}040$ for 198 parameters, $R_w = 0{\cdot}062$. Block-diagonal approximation, $\sum w(\Delta F)^2$ minimized, $w = 1/\sigma^2(F)$ with $\sigma(F) = R_i/|F_o|$ (Seal & Roy, 1981). Standard deviation of observation with unit weight = 0·290. Burroughs 6700 computer (Regional Computer Centre, Calcutta), modified versions of *MAMIE* and *BLOCK* from the *XRAY ARC* program system (Vickery, Bright & Mallinson, 1973).[‡]

---

[*] Department of Chemistry, Jadavpur University, Calcutta-700032, India.

[†] To whom correspondence should be addressed.

[‡] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39754 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/85/010142-03$01.50