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.

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

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**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; $h = 0$–$\pm 7$, $k = 0$–$13$, $l = 0$–$16$; 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 $\Delta F$ synthesis, others, associated with benzene ring, calculated from trigonal geometry around C atoms] isotropic. Max. and min. heights in final difference Fourier map $\pm 0{\cdot}2$ e Å$^{-3}$, max. $\Delta/\sigma$ 0·485, av. $\Delta/\sigma$ 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).‡

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‡ 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.

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**Discussion.** The molecular packing is illustrated in Fig. 1, the atomic coordinates are listed in Table 1 and interatomic distances and angles in Table 2. The molecules are nearly planar and this configuration seems to be stabilized by the intramolecular hydrogen bonding between N(3) and O(1). The phenyl rings make a dihedral angle of 6·7 (1)° with one another. While the O(1)N(1)N(2)N(3) system is quite planar, C(5)N(3)N(2)N(1) deviates significantly [since $(\Delta/\sigma)^2 = 229$] from planarity. The phenyl ring attached to N(1) deviates from the O(1)N(1)N(2)N(3) plane by 12·8 (1)° and that attached to N(3) from C(5)N(3)N(2)N(1) by 8·28 (1)°. The N(1)—N(2) distance [1·280 (2) Å] is much shorter than N(2)—N(3) [1·328 (3) Å], which shows double-bond character in the former and single-bond in the latter. The C(9)—N(1) distance [1·443 (3) Å] is also observed to be appreciably longer than the C(5)—N(3) distance [1·400 (3) Å]. These differences in the C—N bond distances can be explained from the N—N bond orders and non-coplanarity of the phenyl rings with respect to the central part of the molecule. The double-bond character in N(1)—N(2) and the attachment of negatively charged O(1) on N(1) develop a positive charge on the latter in the tetracovalent state. This, together with the non-coplanarity of O(1)N(1)N(2)N(3) with respect to the C(7)···C(12) phenyl ring, makes conjugation less effective between N(1) and this phenyl ring with retention of single-bond character in C(9)—N(1). On the other hand, the tricovalent nature of N(3) and the smaller deviation of the C(1)···C(6) phenyl ring from the C(5)N(3)N(2)N(1) system lead to more effective conjugation in this part of the molecule and a relatively higher double-bond character in the C(5)—N(3) bond. This causes the C(9)—N(1) bond to be longer than C(5)—N(3). Although X-ray crystal structure data of any free triazene or triazene 1-oxide ligand are not available in the literature [except for our previous work (Sarkar *et al.*, 1983)], the above N—N and C—N bond distances find support from those found in the triazene 1-oxide moiety complexed with metals (Dwivedi & Srivastava, 1971; Rajshekharan, Varughese & Monoharan, 1979). This points to the triazene 1-oxide bonding mode >N—N=N(O) with >N→O and >N—H groups in the triazene molecule as opposed to the hydroxytriazene mode —N=N—N(OH)—.

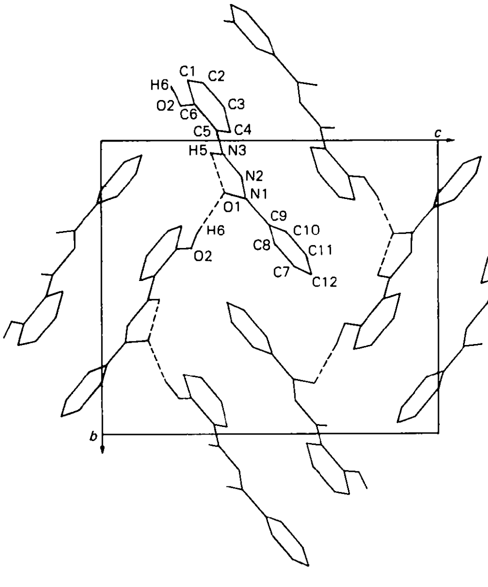

Fig. 1. Projection of the structure on the *bc* plane.

Table 1. *Final atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic temperature factors for* C, N *and* O

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}a_i^*a_i^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| C(1) | 1·2223 (4) | −0·2024 (2) | 0·2551 (2) | 3·8 |
| C(2) | 1·4210 (3) | −0·1953 (2) | 0·2989 (2) | 3·6 |
| C(3) | 1·4743 (3) | −0·1085 (2) | 0·3619 (2) | 3·5 |
| C(4) | 1·3319 (3) | −0·0277 (2) | 0·3818 (2) | 3·2 |
| C(5) | 1·1348 (3) | −0·0343 (2) | 0·3390 (1) | 2·8 |
| C(6) | 1·0794 (3) | −0·1225 (2) | 0·2746 (2) | 2·9 |
| C(7) | 0·7467 (4) | 0·4323 (2) | 0·5778 (2) | 4·5 |
| C(8) | 0·7261 (4) | 0·3452 (2) | 0·5115 (2) | 3·7 |
| C(9) | 0·8961 (3) | 0·2833 (2) | 0·4944 (1) | 3·0 |
| C(10) | 1·0867 (4) | 0·3068 (2) | 0·5405 (2) | 3·6 |
| C(11) | 1·1013 (4) | 0·3948 (2) | 0·6062 (2) | 4·4 |
| C(12) | 0·9341 (5) | 0·4570 (2) | 0·6249 (2) | 4·6 |
| N(1) | 0·8731 (3) | 0·1931 (1) | 0·4246 (1) | 2·8 |
| N(2) | 1·0218 (3) | 0·1240 (1) | 0·4214 (1) | 3·0 |
| N(3) | 0·9834 (3) | 0·0451 (2) | 0·3544 (1) | 3·2 |
| O(1) | 0·7065 (2) | 0·1843 (1) | 0·3677 (1) | 3·6 |
| O(2) | 0·8840 (2) | −0·1220 (1) | 0·2341 (1) | 4·0 |

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

| | | | |
|---|---|---|---|
| C(1)—C(2) | 1·394 (3) | C(11)—C(12) | 1·367 (4) |
| C(2)—C(3 | 1·377 (3) | C(7)—C(12) | 1·374 (4) |
| C(3)—C(4) | 1·384 (3) | C(9)—N(1) | 1·443 (3) |
| C(4)—C(5) | 1·380 (3) | N(1)—N(2) | 1·280 (2) |
| C(5)—C(6) | 1·404 (3) | N(2)—N(3) | 1·328 (3) |
| C(6)—C(1) | 1·378 (3) | N(3)—C(5) | 1·400 (3) |
| C(7)—C(8) | 1·384 (4) | N(1)—O(1) | 1·298 (2) |
| C(8)—C(9) | 1·375 (3) | C(6)—O(2) | 1·356 (3) |
| C(9)—C(10) | 1·384 (3) | O(1)—H(5) | 2·028 (26) |
| C(10)—C(11) | 1·386 (4) | N(3)—O(1) | 2·476 (2) |
| C(6)—C(1)—C(2) | 120·1 (2) | N(2)—N(1)—C(9) | 117·6 (2) |
| C(1)—C(2)—C(3) | 119·9 (2) | N(2)—N(1)—O(1) | 122·2 (2) |
| C(2)—C(3)—C(4) | 120·4 (2) | O(1)—N(1)—C(9) | 120·2 (2) |
| C(3)—C(4)—C(5) | 120·0 (2) | C(8)—C(9)—N(1) | 118·2 (2) |
| C(4)—C(5)—C(6) | 119·9 (2) | N(1)—C(9)—C(10) | 119·9 (2) |
| C(5)—C(6)—C(1) | 119·7 (2) | C(8)—C(9)—C(10) | 121·9 (2) |
| C(6)—C(5)—N(3) | 116·8 (2) | C(9)—C(10)—C(11) | 117·7 (2) |
| C(5)—C(6)—O(2) | 116·4 (2) | C(10)—C(11)—C(12) | 121·4 (2) |
| C(4)—C(5)—N(3) | 123·3 (2) | C(11)—C(12)—C(7) | 119·8 (3) |
| C(5)—N(3)—N(2) | 119·2 (2) | C(12)—C(7)—C(8) | 120·5 (2) |
| N(3)—N(2)—N(1) | 112·1 (2) | C(7)—C(8)—C(9) | 118·7 (2) |
| N(3)—H(5)—O(1) | 108 (2) | | |

The O(1) atom while forming an intramolecular hydrogen bond with N(3) [N(3)—H(5)···O(1) = 2·476 (3) Å] forms another intermolecular hydrogen bond with a second symmetry-related molecule [O(1)···H(6)—O(2) ($\tfrac{3}{2} - x, \tfrac{1}{2} + y, \tfrac{1}{2} - z$) = 2·738 (2) Å] and the

O(1) atom of this second molecule in turn is linked with a third molecule, producing a chain-like structure. The structural analysis thus confirms the *N*-oxide form of triazene and both intra- and intermolecular hydrogen bonds.

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# Absolute Configuration of (—)-Methyl 2-(4-Bromobenzylsulfinyl)benzoate, $C_{15}H_{13}BrO_3S$

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**Abstract.** $M_r = 353\cdot22$, monoclinic, $P2_1$, $a = 12\cdot081\,(2)$, $b = 5\cdot740\,(1)$, $c = 12\cdot956\,(2)$ Å, $\beta = 122\cdot48\,(2)$°, $V = 757\cdot9\,(3)$ Å$^3$, $Z = 2$, $D_m = 1\cdot51$, $D_x = 1\cdot548$ Mg m$^{-3}$, Mo $K\alpha$, $\lambda = 0\cdot71093$ Å, $\mu = 2\cdot76$ mm$^{-1}$, $F(000) = 356$, room temperature, $R = 0\cdot060$ for 3228 unique reflections and 181 parameters. The absolute configuration of the chiral S atom was established as *S*. The S—O bond with respect to the methoxycarbonyl group is in the *transoid* conformation. The conformation around the S—C(7) bond is *sc–sc*. An interaction occurs between the substituents of the *para*-substituted benzene ring. The methoxycarbonyl group is involved in two short intermolecular contacts.

**Introduction.** The problem of the effect of position isomerism of certain substituents in aromatic rings on optical properties of aromatic–aliphatic systems containing heteroatomic chirality centers separated from aromatic fragments of the molecule by methylene groups has been examined in our laboratory. The observed optical order in the group of isomeric bromobenzylsulfinylacetic acids (Janczewski, Księżopolski & Rak-Najda, 1981; Janczewski & Księżopolski, 1984) as well as in the group of isomeric methylbenzylsulfinylacetic acids (Janczewski & Janowski, 1978) suggested that a single methylene group does not isolate completely the chiral sulfoxide system from the effects caused by introduction of substituents on an aromatic ring. The observed optical and stereochemical relationships encouraged us to further studies in the group of isomeric 2-(bromobenzylsulfinyl)benzoic acids.

The unsubstituted 2-(benzylsulfinyl)benzoic acid (Janczewski, Majewski, Radkiewicz & Grzegórski, 1983) was assumed as a reference system having the standard type of configuration as well as being a standard for comparing the measured rotation values. Crystals of this compound were of poor quality; only (—)-methyl 2-(4-bromobenzylsulfinyl)benzoate (Janczewski, Jurczak & Majewski, 1984) crystals could be used for X-ray analysis. It was found on the basis of the Freudenberg optical shift rule and the comparison of ORD and CD spectra that the optically active 2-(benzylsulfinyl)- and 2-(4-bromobenzylsulfinyl)benzoic acids with the same direction of molar rotation have the same spatial structure. Therefore, the present determination of absolute configuration of (—)-2-(4-

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