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Structure of Liquid Crystalline 1-Phenyl-3-{4-[4-(4-octyloxybenzoyloxy)phenyloxycarbonyl]phenyl}triazene-1-oxide at Low Temperature

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The molecular structure of 1-phenyl-3-{4-[4-(4-octyloxybenzoyloxy)-phenyloxycarbonyl]phenyl}triazene-1-oxide, a member of newly developed liquid crystalline homologous series, has been investigated by crystal X-ray crystallography at low temperature (100 K). The title compound crystallizes in the triclinic crystal class in the space group $P\bar{1}$ *with cell parameters* $a = 5.766(5)$ Å, $b = 12.151(10)$ Å, $c = 21.751(17)$ Å, $\alpha = 79.089(13)^\circ$, $\beta = 88.646(14)^\circ$, $\gamma = 84.278(14)^\circ$, $V = 1489(2)$ Å^3 *for* $Z = 2$. *It establishes the* N*-oxide form of the triazene-1-oxide moiety. The overall molecule is not planar, the dihedral angles between pairs of adjacent benzene rings are 14.00 (10), 52.36 (07), and 50.57 (07)°. Intramolecular N–H···O hydrogen-bonding is present within the triazene-1-oxide moiety of the title compound. The compound forms inversion dimer* via *an intermolecular N–H···O and an intermolecular C–H···O links. The dimers are then linked into chains in a parallel fashion by C–H···O hydrogen bonds. The crystal packing is further stabilized by C–H···π interactions.*

Keywords: hydrogen-bonding interaction; liquid crystals; triazene-1-oxide; X-ray crystallography

INTRODUCTION

Arytriazene-1-oxides and their substituted derivatives are well known for their excellent metal binding properties [1–3] and their

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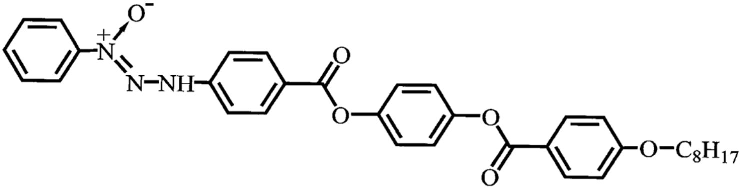
metallo-derivatives find applications in analytical chemistry [4–6] and catalysis [7]. A group of triazene-1-oxides viz 3-aryltriazene-1-oxide, (pyridyl)triazene-1-oxide, and 1-(4-carbamoylphenyl)-3,3-dimethyltriazene-1-oxide are reported to be biologically active [8,9]. Unlike aryldiazene-1-oxides or azoxybenzenes [10], the mesogenic behavior of triazene-1-oxides or their substituted derivatives remained unexplored. Recently, we have initiated a program to develop mesogenic triazene-1-oxides with suitable structural modifications. We have successfully designed and synthesized two liquid crystalline homologous series viz 1-phenyl-3-{4-[4-(4-*n*-alkoxybenzoyloxy)-phenyloxycarbonyl]phenyl}-triazene-1-oxide [11] and 3-(4′-(4″-imino(4‴-(*n*-alkyloxy)phenyl)-phenyl)carboxylatophenyl)-1-phenyltriazene-1-oxide [12].

The knowledge of the molecular geometry and packing of the molecules in crystalline state often provide better understanding of the observed phase behavior, which depends on subtle balance of intermolecular interactions [13,14]. With this aim, we attempted to determine the structure of 1-phenyl-3-{4-[4-(4-nonyloxybenzoyloxy)phenyloxycarbonyl]phenyl}-triazene-1-oxide at room temperature, which resulted in very high R factor (15.07%) [11]. Our endeavor with 1-phenyl-3-{4-[4-(4-undecyloxybenzoyloxy)phenyloxycarbonyl] phenyl}triazene-1-oxide at 150 K also met with high R factor (9.6%) [15]. This has prompted us to collect the X-ray diffraction data at moderately low temperature. Herein we wish to report the molecular structure of 1-phenyl-3-{4-[4-(4-octyloxybenzoyloxy)phenyloxycarbonyl]phenyl}-triazene-1-oxide (**I**) at low temperature (100 K).



(**I**)

EXPERIMENTAL

The title compound, 1-phenyl-3-{4-[4-(4-octyloxybenzoyloxy)phenyloxy-carbonyl]phenyl}-triazene-1-oxide (**I**) was synthesized by coupling nitrobenzene, *p*-aminobenzoic acid, hydro-quinone, and *p*-octyloxy-benzoic acid following the reported method [11]. Its spectral data and mesogenic properties have been described elsewhere [11]. The compound (**I**) was crystallized by the slow diffusion of its dichloromethane solution into aqueous ethanol. A needle-shaped crystal of dimensions

$0.24 \times 0.18 \times 0.08\,\mathrm{mm}^3$ (approximately) was chosen for X-ray diffraction data collection. The data were collected on a Bruker SMART APEX CCD area detector diffractometer at 100(2) K by the φ and ω scan method using graphite-monochromated Mo Kα radiation. A total of 11564 unique reflections were measured within the range $-7 \le h \le 7$, $-14 \le k \le 14$, $-26 \le l \le 26$. Of these, 5756 were above the significance level of $2\sigma(I)$. The structure was solved by direct methods using SHELXS-97 and difference Fourier syntheses. Full-matrix-least-squares structure refinement against $|F^2|$ was carried out. Bruker SMART [16] was used for the data collection. Cell refinement and data reduction were done using Bruker SAINT [17]. Absorption correction was done by multiscan method using SADABS [18]. The structure was solved by direct method and refined using SHELXS97 and SHELXL97 [19], respectively. The N-bound H atom was located in a difference Fourier map, and its coordinates and isotropic displacement parameter were freely refined. C-bound H atoms were included at calculated positions as riding atoms with C–H set to 0.95 Å for (aromatic), 0.98 Å for (CH_3), and 0.99 Å for (CH_2) H atoms, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ ($1.5U_{\mathrm{eq}}$ for methyl group). SHELXTL [20] was used for the molecular graphics and to prepare the material for publication.

CRYSTAL STRUCTURE DETERMINATION

The molecular structure of the title compound, (**I**), has been shown in Fig. 1, with the atom-numbering scheme. The crystal and structure refinement data for compound (**I**) is summarized in Table 1. The atomic coordinates and equivalent thermal parameters of the nonhydrogen atoms are collected in Table 2. Selected bond lengths, bond angles, and torsion angles are given in Table 3.

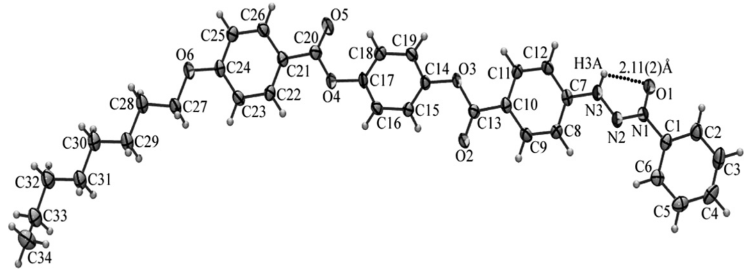


FIGURE 1 The asymmetric unit of (**I**), with displacement ellipsoids drawn at the 75% probability level. Dotted lines indicate the intramolecular N–H···O interaction.

TABLE 1 Crystal Data and Structure Refinement Table

CCDC deposition number	692312
Empirical formula	$C_{34}H_{35}N_3O_6$
Formula weight	581.65
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 5.766(5)$ Å
	$b = 12.151(10)$ Å
	$c = 21.751(17)$ Å
	$\alpha = 79.089(13)^\circ$
	$\beta = 88.646(14)^\circ$
	$\gamma = 84.278(14)^\circ$
Volume	1489(2) $Å^3$
Z	2
Calculated density	1.297 Mg/m^3
Absorption coefficient	0.090 mm^{-1}
F(000)	616
Crystal size	0.24 × 0.18 × 0.08 mm
Theta range for data collection	0.95° to 26.00°
Limiting indices	$-7 \leq h \leq 7$
	$-14 \leq k \leq 14$
	$-26 \leq l \leq 26$
Reflections collected	11564
Independent reflections	5756 [R(int) = 0.0475]
Absorption correction	multiscan
Refinement method	Full-matrix least-squares on F2
Data/restraints/parameters	5756/0/393
Goodness-of-fit on F^2	.057
Final R indices [I > 2sigma(I)]	$R1 = 0.0510$, $wR2 = 0.1293$
R indices (all data)	$R1 = 0.0639$, $wR2 = 0.1421$
Largest diff. peak and hole	0.277 and −0.309 e.$Å^{-3}$

The planar phenyl moiety and trigonal planar geometry of the triazene N3 atom strongly suggest a resonance interaction extending over the C1, N1, N2, and N3 atoms. The overall molecule is not planar the benzene rings C1–C6 (*A*), C7–C12 (*B*), C14–C19 (*C*), and C21–C26 (*D*) are inclined to each other in a way that the dihedral angles between pairs of adjacent benzene rings *A*/*B*, *B*/*C*, and *C*/*D* are 14.00 (10), 52.36 (07), and 50.57 (07)°, respectively. The N1−N2 and N2−N3 distances (Table 3) are in good agreement with the reported values of other triazene-1-oxides [11,15,21,22]. The shorter length of N1–N2 indicates its double-bond character, and the longer N2–N3 distance is still shorter than a pure single-bond (Table 3). The deviation of O1 from the molecular plane causes conjugation between N1−C1 to

TABLE 2 Atomic Coordinates and Equivalent Thermal Parameters of the Nonhydrogen Atoms

Atom	x	y	z	U(eq)
O(1)	3042(2)	−923(1)	32(1)	24(1)
O(2)	−10(2)	4351(1)	2332(1)	23(1)
O(3)	3441(2)	4866(1)	1913(1)	21(1)
O(4)	3204(2)	8812(1)	2849(1)	24(1)
O(5)	6233(2)	9407(1)	2242(1)	32(1)
O(6)	3349(2)	13622(1)	3532(1)	25(1)
N(1)	1538(2)	−965(1)	482(1)	19(1)
N(2)	1302(3)	−253(1)	850(1)	21(1)
N(3)	2770(3)	543(1)	715(1)	21(1)
C(1)	17(3)	−1858(1)	599(1)	21(1)
C(2)	736(3)	−2854(2)	396(1)	26(1)
C(3)	−695(4)	−3724(2)	519(1)	34(1)
C(4)	−2801(4)	−3594(2)	830(1)	32(1)
C(5)	−3488(3)	−2585(2)	1023(1)	28(1)
C(6)	−2083(3)	−1709(2)	912(1)	23(1)
C(7)	2483(3)	1446(1)	1032(1)	20(1)
C(8)	512(3)	1616(1)	1400(1)	24(1)
C(9)	306(3)	2528(1)	1699(1)	24(1)
C(10)	2015(3)	3269(1)	1646(1)	20(1)
C(11)	3976(3)	3094(1)	1275(1)	22(1)
C(12)	4211(3)	2187(1)	969(1)	23(1)
C(13)	1651(3)	4198(1)	2000(1)	18(1)
C(14)	3277(3)	5838(1)	2181(1)	19(1)
C(15)	1344(3)	6629(1)	2075(1)	20(1)
C(16)	1373(3)	7628(1)	2294(1)	21(1)
C(17)	3307(3)	7809(1)	2613(1)	20(1)
C(18)	5223(3)	7013(1)	2720(1)	21(1)
C(19)	5206(3)	6011(1)	2503(1)	20(1)
C(20)	4728(3)	9576(1)	2616(1)	22(1)
C(21)	4280(3)	10610(1)	2882(1)	19(1)
C(22)	2259(3)	10855(1)	3210(1)	21(1)
C(23)	1878(3)	11850(1)	3435(1)	22(1)
C(24)	3553(3)	12618(1)	3333(1)	20(1)
C(25)	5602(3)	12383(1)	3007(1)	23(1)
C(26)	5945(3)	11388(1)	2784(1)	22(1)
C(27)	1170(3)	13943(1)	3818(1)	24(1)
C(28)	1165(3)	15140(1)	3914(1)	27(1)
C(29)	−1192(3)	15551(1)	4165(1)	26(1)
C(30)	−1358(3)	16779(2)	4245(1)	28(1)
C(31)	−3776(3)	17219(2)	4444(1)	29(1)
C(32)	−3991(3)	18472(2)	4473(1)	31(1)
C(33)	−6464(3)	18949(2)	4612(1)	30(1)
C(34)	−7308(4)	18523(2)	5271(1)	37(1)

$U_eq = (1/3)\sum_i \sum_j U_ij(a_i^* a_j^*)\ (\mathrm{a_i} \cdot \mathrm{a_j})$.

TABLE 3 Selected Bond Lengths [Å] Bond Angles [°] and Torsion Angles [°]

O(1)–N(1)	1.2888 (18)	N(2)–N(3)	1.335 (2)
N(1)–N(2)	1.281 (2)	N(3)–C(7)	1.398 (2)
N(1)–C(1)	1.445 (2)	N(3)–H(3A)	0.93 (2)
O(1)–N(1)–N(2)	123.74 (14)	O(1)–N(1)–C(1)	120.08 (13)
N(2)–N(1)–C(1)	116.18 (14)	N(1)–N(2)–N(3)	112.72 (14)
N(2)–N(3)–C(7)	117.96 (15)	N(2)–N(3)–H(3A)	117.9 (13)
C(7)–N(3)–H(3A)	123.7 (13)	C(6)–C(1)–N(1)	119.93 (15)
C(2)–C(1)–N(1)	118.04 (16)	C(8)–C(7)–N(3)	121.18 (16)
C(12)–C(7)–N(3)	118.42 (16)		
O(1)–N(1)–N(2)–N(3)	0.5 (2)	C(1)–N(1)–N(2)–N(3)	179.73 (13)
N(1)–N(2)–N(3)–C(7)	172.10 (13)	O(1)–N(1)–C(1)–C(2)	23.6 (2)
N(2)–N(1)–C(1)–C(6)	23.8 (2)	O(1)–N(1)–C(1)–C(6)	−156.95 (15)
N(2)–N(1)–C(1)–C(2)	−155.59 (15)	N(2)–N(3)–C(7)–C(8)	−10.5 (2)
N(2)–N(3)–C(7)–C(12)	170.06 (14)	C(13)–O(3)–C(14)–C(15)	−52.8 (2)
C(13)–O(3)–C(14)–C(19)	132.76 (16)	C(20)–O(4)–C(17)–C(18)	66.8 (2)
C(20)–O(4)–C(17)–C(16)	−116.14 (18)		

be less effective and is reflected in the longer N1-C1 than N3–C7 distance (Table 3). There is an intramolecular N–H···O interaction within the triazene-1-oxide moiety (Fig. 1, Table 4). The intramolecular hydrogen bondings result almost planar conformation of the triazene fragment of the molecule.

The molecular packing of (**I**) has been shown in Fig. 2. The intermolecular hydrogen bonding causes dimer formation of (**I**) (Fig. 3). C16 and C19 atoms in the molecule at (x, y, z) of (**I**) act as hydrogen-bond donor via H16 and H19 to O5 atom at (x + 1, y, z) and O2 atom at (x−1, y, z), respectively, to form a two-dimensional sheet structure (Fig. 4, Table 4). The asymmetric unit of (**I**) is further linked to the molecules

TABLE 4 Hydrogen-Bond Geometry (Å, °)

D—*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3A···O1	0.93 (2)	2.11 (2)	2.517 (3)	104.8 (17)
N3—H3A···O1$^{\mathrm{i}}$	0.93 (2)	2.08 (2)	2.905 (3)	147.3 (19)
C12—H12···O1$^{\mathrm{i}}$	0.95	2.41	3.198 (3)	140
C16—H16···O5$^{\mathrm{ii}}$	0.95	2.55	3.481 (4)	168
C19—H19···O2$^{\mathrm{iii}}$	0.95	2.41	3.309 (4)	158
C27—H27B···O2$^{\mathrm{iv}}$	0.99	2.59	3.255 (4)	124
C5—H5···Cg3$^{\mathrm{v}}$	0.95	2.72	3.480 (4)	137
C15—H15···Cg1$^{\mathrm{iv}}$	0.95	2.61	3.311 (3)	131
C28—H28A···Cg3$^{\mathrm{iv}}$	0.99	2.81	3.783 (4)	169

Symmetry codes: (i) $-x+1, -y, -z$; (ii) $x-1, y, z$; (iii) $x+1, y, z$; (iv) $x, y+1, z$; (v) $x-1, y-1, z$.

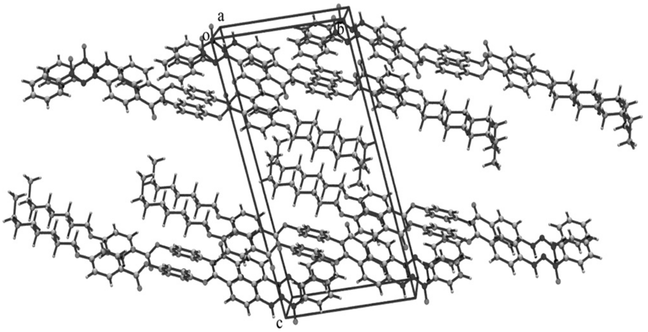


FIGURE 2 The molecular packing of (**I**) showing the arrangements of the molecules in the *bc*-plane.

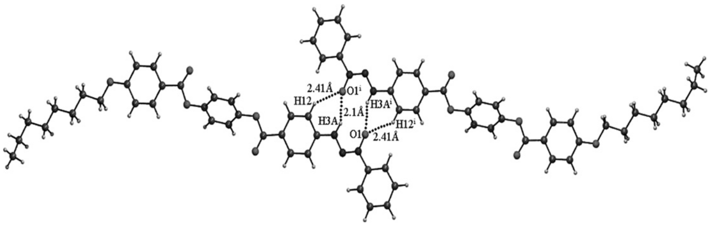


FIGURE 3 Dimerization of two molecules (**I**) through intermolecular N–H ⋯ O and C–H ⋯ O hydrogen bonding interactions shown by dotted lines (Symmetry code: (i) −x + 1, −y, −z + 2).

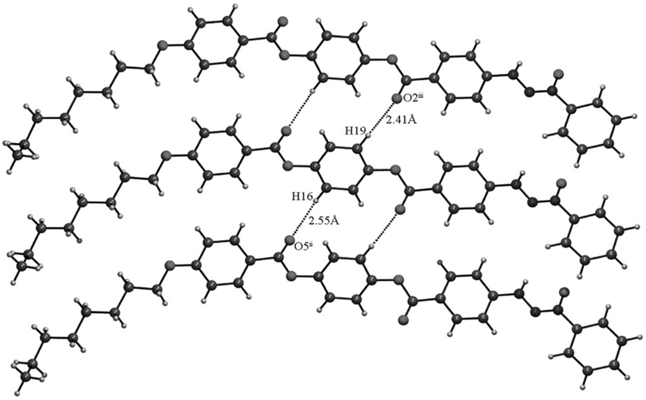


FIGURE 4 Parallel arrangement of (**I**) through intermolecular C–H ⋯ O interactions shown by dotted lines (Symmetry codes: (ii) x + 1, y, z; (iii) x−1, y, z).

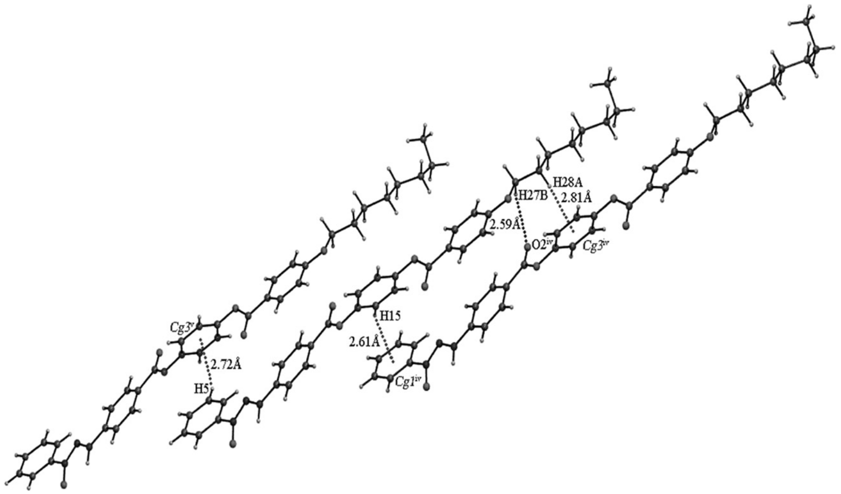


FIGURE 5 Parallel arrangement of (**I**) through intermolecular C−H $\cdots\pi$ interactions shown by dotted lines (Symmetry codes: (iv) x−1, y + 1, z; (v) x, y−1, z. *Cg*1 and *Cg*3 are the centroids of the C1–C6 and C14–C19 rings, respectively).

at (x−1, y + 1, z) and at (x, y−1, z) through C–H $\cdots\pi$ interactions to form a layer like assembly (Fig. 5, Table 4) [23].

CONCLUSIONS

The molecular structure of the title compound (**I**) has been understood by the X-ray diffraction study. The X-ray data collection of the title compound at low temperature (100 K) afforded satisfactory R factor of 5.1%. There is an intramolecular N–H $\cdots$ O hydrogen-bonding interaction within the triazene-1-oxide moiety of (**I**). The intermolecular N−H $\cdots$ O and C−H $\cdots$ O interactions cause dimer formation in (**I**). The intermolecular C−H $\cdots$ O and C−H $\cdots\pi$ interactions hold the phenyl triazene-1-oxide fragments of (**I**) in layer arrangement within the molecular assembly.

SUPPLEMENTARY MATERIALS

Crystallographic data for structural analysis of (**I**) has been deposited at the Cambridge Crystallographic Data Center, CCDC, No. 692312. Copies of this information can be obtained from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1233 336033; E-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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