the *ORTEP* drawings of the two independent molecules and numbering of atoms. Most equivalent bond lengths and bond angles in both independent molecules agree to within 0·015 Å and 1·0°. Greater variations occur for the N(3)—C(2) bond length (4σ), and O(2)—N(3)—O(3) and O(3)—N(3)—C(2) bond angles (4σ). Fixation of double bonds in the six-membered ring definitely occurs in the title compound. Moreover, the N—O and C—N bond lengths in the five-membered ring agree with those of a standard single bond for N—O and a double bond for C—N, respectively. This shows that the π-electron delocalization in the BFZ skeleton is very small.

The BFZ skeleton is almost planar. The Cl atom is coplanar with the BFZ skeleton [the deviation from the least-squares plane of the BFZ skeleton is 0·009 (1) Å for molecule (I) and 0·019 (2) Å for molecule (II), respectively] while the nitro group deviates upward from it {the average and maximum deviations are 0·081 (3), 0·101 (5) Å [atom O(2)] for molecule (I), and 0·096 (3), 0·166 (5) Å [atom O(2)] for molecule (II), respectively}. The difference in the dihedral angles between the least-squares plane of the BFZ skeleton and that of the nitro group is too small to cause the observed variation in the N(3)—C(2) bond length between molecules (I) and (II).

Examination of the packing diagram (Fig. 2) reveals that only the $\mathrm{N(1^{i})\cdots Cl^{ii}}$ [(i) x, $y-\frac{1}{2}$, $1-z$; (ii) x, y, z] distance [3·262 (5) Å] is shorter than the corresponding van der Waals distance (3·30 Å). However, there are seven intermolecular distances longer than the corresponding van der Waals distance within 0·2 Å. The difference in the structures of the two independent molecules may originate from intermolecular interactions related to these atomic pairs. The greater variations in the bond length and bond angles for the nitro group may be mainly caused by the $\mathrm{O(2^{i})\cdots C(2^{ii})}$ [(i) x, y, z; (ii) $x-1$, y, z] interaction, whose intermolecular distance [3·131 (8) Å] is nearly equal to the corresponding van der Waals distance (3·10 Å), and the more flexible character of the nitro group than that of the rest of the molecule. The $\mathrm{Cl^{i}\cdots Cl^{ii}}$ [(i) x, y, z; (ii) x, y, z] distance in the asymmetric unit [3·639 (2) Å] is nearly equal to the corresponding van der Waals distance (3·60 Å), while other Cl···Cl distances are longer than 4·0 Å.

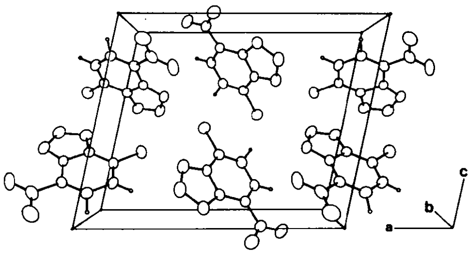

Fig. 2. Packing diagram viewed along the *b* axis.

The noncentrosymmetric crystal structure is consistent with the observation of second-harmonic generation.

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Acta Cryst. (1988). C**44**, 486–489

(*Z*,*Z*)-1,1′-(1,6-Hexanediyl)bis(2-phenyldiazene) 2,2′-Dioxide:* A Bis(azoxy) Compound

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(*Received 26 June* 1987; *accepted 9 October* 1987)

Abstract. $\mathrm{C_{18}H_{22}N_4O_2}$, $M_r = 326{\cdot}40$, orthorhombic, *Pbca*, $a = 19{\cdot}475\ (10)$, $b = 10{\cdot}435\ (20)$, $c = 8{\cdot}762\ (20)$ Å, $V = 1780{\cdot}6$ Å^3, $Z = 4$, $D_x = 1{\cdot}22$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}76$ cm^{-1}, $F(000) = 696$, room temperature, 1564 reflections averaged from two octants, $R = 0{\cdot}044$, $wR = 0{\cdot}050$ for

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* Alternative name: 1,6-bis(phenyl-*ONN*-azoxy)hexane.

669 observed reflections with $I > \sigma(I)$. The molecule has inversion symmetry and is nearly planar. The azoxy group is *trans*-substituted. Molecular packing is in herringbone-type layers.

Introduction. Diazene oxides form an important class of molecules related to diazenes and hydrazenes (Patai, 1975). Yandovskii, Gidaspov & Tselinskii (1981) have reviewed the oxidative synthesis of diazene oxides and provide 352 references to the literature. Bystroem (1983) made a molecular-mechanics study of several azoxy molecules in order to predict their structure and to understand their higher stability relative to the non-oxygenated diazenes. As with diazenes, the substituents on the azoxy group can be *cis* or *trans*. We are synthesizing bis(azoxy) compounds as models of liquid-crystal polymers having main-chain spacers between the mesogenic groups (Ober, Jin & Lenz, 1984), and we are examining their crystal packing for dipolar ordering.

Experimental. Synthesis of the title compound was accomplished using the method of Nelson, Serianz & Kovacic (1976). Chromatography over silica gel and two recrystallizations from petroleum ether yielded white crystals, m.p. 347–348 K, ^{1}H NMR ($CDCl_3$) δ 8·14 (*m,o*-Ph), 7·49 (*m,m,p*-Ph), 3·68 (*t*,NCH_2), 1·90 (*m*,NCH_2CH_2), 1·58 [$N(CH_2)_2CH_2$]. Recrystallization from methanol gave crystals suitable for X-ray diffraction. X-ray diffraction data were obtained with an Enraf–Nonius CAD-4H diffractometer equipped with an incident-beam graphite monochromator from a plate-shaped colorless crystal 0·1 × 0·25 × 0·25 mm glued on a glass fiber. The cell dimensions were taken from a least-squares fit to 25 reflections. The space group was uniquely determined from the observed extinctions ($0kl$: $k = 2n + 1$; $h0l$: $l = 2n + 1$; $hk0$: $h = 2n + 1$). A total of 3430 reflections were measured with an $\omega/2\theta$ scan; the ω-scan width was $(0·6 + 0·34\tan\omega)^\circ$; the maximum θ was 25°. Three reference reflections were remeasured every 3 h of exposure; no significant change in intensity occurred. Intensities were corrected for Lp and equivalent reflections averaged to give 1564 unique reflections, of which 669 had $I > \sigma(I)$. The structure was solved by direct methods using *MULTAN*82 (Main, 1982); all nonhydrogen atoms were located from an E map prepared from the phase set with the highest figure of merit. Refinement was by full-matrix least squares with H atoms placed in calculated positions, with anisotropic temperature factors for the heavy atoms. H atoms were assigned fixed isotropic temperature factors whose values were 1·3 times the averaged B values of the heavy atoms to which they were bonded. The final R was 0·044 and wR was 0·050 for 145 variable parameters. In the final cycle the largest parameter shift was 0·02 times its e.s.d. The standard deviation of an observation of unit weight was 0·99. The final difference Fourier map had highest and lowest peaks of 0·16 (4) and −0·15 (4) e Å^{-3}. Final values of the parameters are given in Table 1.*

Discussion. Fig. 1 gives a view of the molecule with the atomic numbering. Bond distances and bond angles are given in Table 2. The molecule has inversion symmetry

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = \tfrac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	B_{eq}(Å^2)
O(1)	0·6237 (1)	0·1880 (2)	0·0481 (2)	6·79 (5)
N(1)	0·6197 (1)	0·0677 (2)	0·0520 (3)	4·36 (5)
N(2)	0·5940 (1)	−0·0030 (2)	−0·0494 (3)	4·82 (5)
C(1)	0·6481 (1)	0·0037 (2)	0·1874 (3)	3·80 (5)
C(2)	0·6754 (1)	0·0778 (2)	0·3001 (3)	4·96 (6)
C(3)	0·7040 (1)	0·0184 (3)	0·4271 (4)	5·87 (7)
C(4)	0·7057 (2)	−0·1133 (3)	0·4368 (4)	5·45 (7)
C(5)	0·6768 (2)	−0·1858 (3)	0·3229 (3)	5·33 (7)
C(6)	0·6476 (2)	−0·1290 (3)	0·1952 (3)	4·61 (6)
C(7)	0·5668 (2)	0·0687 (3)	−0·1796 (3)	5·27 (7)
C(8)	0·5410 (1)	−0·0234 (3)	−0·2985 (3)	4·96 (6)
C(9)	0·5120 (1)	0·0456 (3)	−0·4389 (3)	4·75 (6)

Table 2. *Molecular structure*

(*a*) Bond distances (Å)

O(1)–N(1)	1·258 (3)	C(3)–C(4)	1·378 (4)
N(1)–N(2)	1·259 (3)	C(4)–C(5)	1·373 (4)
N(1)–C(1)	1·470 (3)	C(5)–C(6)	1·388 (5)
N(2)–C(7)	1·463 (4)	C(7)–C(8)	1·504 (4)
C(1)–C(2)	1·363 (4)	C(8)–C(9)	1·533 (4)
C(1)–C(6)	1·386 (3)	C(9)–C(9′)	1·507 (4)
C(2)–C(3)	1·390 (5)		

(*b*) Bond angles (°)

O(1)–N(1)–N(2)	126·2 (2)	C(2)–C(3)–C(4)	120·3 (3)
O(1)–N(1)–C(1)	116·9 (3)	C(3)–C(4)–C(5)	119·6 (3)
N(2)–N(1)–C(1)	116·9 (2)	C(4)–C(5)–C(6)	121·2 (3)
N(1)–N(2)–C(7)	113·2 (3)	C(1)–C(6)–C(5)	117·7 (2)
N(1)–C(1)–C(2)	118·3 (2)	N(2)–C(7)–C(8)	109·5 (2)
N(1)–C(1)–C(6)	119·5 (2)	C(7)–C(8)–C(9)	112·2 (2)
C(2)–C(1)–C(6)	122·3 (2)	C(8)–C(9)–C(9′)	112·8 (2)
C(1)–C(2)–C(3)	118·9 (2)		

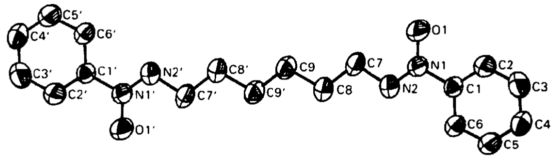

Fig. 1. *ORTEP* plot of the molecule showing the atomic numbering system. The thermal ellipsoids are plotted at the 50% probability level.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, a complete list of bond angles and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44447 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Geometry of the substituted azoxy group*

The reported standard deviations are 0·002–0·007 Å for distances and 0·3–0·6° for angles.

	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)
N=N	1·259	1·273	1·262	1·253	1·269	1·265	1·218	1·155
N–O	1·258	1·262	1·273	1·256	1·251	1·256	1·279	1·291
C–N(O)	1·470	1·467	1·457	1·512	1·560	1·512	1·496	1·570
C–N	1·463	1·456	1·459	1·462	1·475	1·462	1·496	1·559
N–N(O)–O	126·2	124·9	119·9	119·3	124·3	120·5	130·3	134·7
N–N(O)–C	116·9	117·4	126·4	126·0	116·9	125·0	111·8	109·1
O–N(O)–C	116·9	117·7	113·9	114·7	118·8	114·3	117·9	116·2
N(O)–N–C	113·2	111·3	118·9	117·6	107·1	119·2	114·7	113·5

(I) *trans*, this work; (II) *trans*, macrozamin (Cannon, Raston, Toia & White, 1980); (III) *cis*, methyl, cyclohexyl (Baker & Williams, 1977); (IV) *cis*, cyclohexyl, methyl (Baker & Williams, 1977); (V) *cis*, bicyclic (Maverick, Maverick & Olsen, 1980); (VI) *cis*, phenyl, tolyl (Hoesch & Weber, 1977); (VII) *trans*, bis(*p*-methoxyphenyl) (Krigbaum *et al.*, 1970); (VIII) *trans*, bis(*p*-ethoxycarbonylphenyl) (Krigbaum & Barber, 1971).

at the center of the C(9)—C(9′) bond. The benzene ring is planar, with a maximum observed deviation of 0·012 Å from the least-squares plane. The entire carbon framework is also nearly planar, with the largest observed deviations of 0·042 and 0·040 Å being shown by C(4) and N(2). The C—C distances in the benzene ring range from 1·363 Å (conjugated to the N—N double bond) to 1·390 Å. The ring angles show some deviations from a regular hexagon, with the angle at C(1) increasing to 122·3° and the angles at C(2) and C(6) decreasing to 118·9 and 117·7°, respectively. In the hexane moiety the C—C distances are 1·504, 1·533, and 1·507 Å, with the shorter distances being conjugated with the N=N double bond. The hexane C—C—C bond angles are in the expected range at 112·2 and 112·8°.

In the present compound the azoxy group is *trans*-substituted. There are now available several examples of both *cis*- and *trans*-substituted azoxy groups. Table 3 makes a comparison of the azoxy-group geometry in several structures, including this work.

The molecular packing displays herringbone layers (Fig. 2) such as typically found in aromatic hydrocarbon crystals. In this packing type positively charged H atoms are packed close to negatively charged C atoms. The planes of the molecules are very nearly parallel to the **b** direction. The figure shows that the layers are staggered to achieve close packing. In the present structure the polar azoxy groups apparently do not influence the molecular packing very much, and there are no unusually short intermolecular contacts. The shortest intermolecular nonbonded distances by type are: H···H, 2·54; H···C, 3·05; H···N, 2·96; H···O, 2·65; C···C, 3·68; C···N, 3·58; C···O, 3·42 Å; there are no N···N, N···O, or O···O distances below 3·5 Å.

Azoxy compounds which show ordering of the azoxy groups often display mesomorphic properties (Krigbaum, Chatain & Barber, 1970; Krigbaum & Barber, 1971). The title compound is an example of an azoxy compound not exhibiting the dipolar ordering displayed by all other sterically uncrowded azoxy compounds having nonpolar alkyl or aryl substituent groups [entries (III)–(VII), Table 3]. Also, this compound does not display mesomorphic properties.

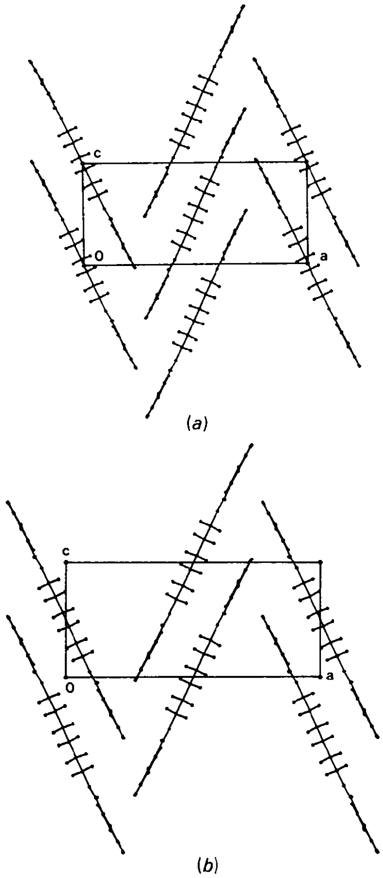

Fig. 2. The molecular packing viewed along **b**. (*a*) Layer at $b = 0$. (*b*) Layer at $b = \frac{1}{2}$.

This work was supported by NIH research grant GM37453.

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Acta Cryst. (1988). C**44**, 489–495

Structure of 21-Acetoxy-11(*R*)-rifamycinol S. The Role of the One- and Two-Phase Semi-invariants in Multisolution Phasing Methods

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(*Received* 29 *April* 1987; *accepted* 18 *September* 1987)

Abstract. $C_{39}H_{49}NO_{13}.CH_3OH.H_2O$, $M_r = 789{\cdot}87$, monoclinic, $P2_1$, $Z = 2$, $F(000) = 844$, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, room temperature; $a = 11{\cdot}860\,(4)$, $b = 9{\cdot}140\,(3)$, $c = 20{\cdot}423\,(4)$ Å, $\beta = 90{\cdot}72\,(2)°$, $U = 2213\,(1)$ Å^3, $D_x = 1{\cdot}18$ Mg m^{-3}, μ(Mo $K\alpha$) = 0·099 mm^{-1}, $R = 0{\cdot}071$, $wR = 0{\cdot}099$ for 4043 observed reflections. The structure was solved by direct methods, using one-phase and two-phase semi-invariants in an active way. An *a posteriori* examination of the convergence/divergence map showed that conventional direct methods failed because of the role played by aberrant triplet relationships in the very early stages of the phase-extension procedure. The conformational stability of the ansa-bridge, as observed in many active rifamycin derivatives, is unaffected in this new derivative by the acetylation at O(10) and the reduction at C(11). Nevertheless the acetylation at O(10) does prevent biological activity.

Introduction. Rifamycins are a class of natural and semi-synthetic antibiotics very active on Gram-positive bacteria and mycobacteria; they act as inhibitors of the bacterial enzyme DNA-dependent RNA polymerase (Hartmann, Honikel, Knusel & Nuesch, 1967; Umezawa, Mizuno, Yamazaki & Nitta, 1968).

Many active derivatives of the natural compounds have been studied in the solid state: rifamycin B *p*-iodoanilide (RIFB) (Brufani, Cerrini, Fedeli & Vaciago, 1974), rifampicin (RIFMP) (Gadret, Goursolle, Leger & Colleter, 1975), 3-methoxycarbonylrifamycin S (RIFCM) (Cellai, Cerrini, Segre, Brufani, Fedeli & Vaciago, 1982*a*), rifamycin SV (RIFSV) (Arora, 1983), rifamycin S (RIFAS) (Arora, 1985), and rifamycinol (RIFOLS) (Cellai, Cerrini, Lamba, Brizzi & Brufani, 1987).

Structure–activity relationships based on structural investigations (Brufani, Cerrini, Fedeli & Vaciago, 1974; Brufani, Cellai, Cerrini, Fedeli & Vaciago, 1978) suggested the basic three-dimensional requirements for biological activity. They are: (i) the presence at the chromophoric nucleus of two oxygenated functions at C(1) and C(8), the former either in the quinone form (rifamycin S) or as free hydroxyl (rifamycin SV), the latter as free hydroxyl; (ii) the presence at the ansa-chain of two free hydroxyl groups at C(21) and C(23); (iii) the conformation of the ansa-chain being such that the spatial arrangement of the oxygenated functions is suitable for hydrogen-bond interactions.

Recently, ^{1}H NMR studies have been carried out, both in water and organic solvents, on many 3-substituted rifamycin S and SV derivatives (Cellai, Cerrini, Segre, Brufani, Fedeli & Vaciago, 1982*b*). It transpires that the oxygen atoms O(1), O(2), O(9) and O(10) show the same spatial arrangement that has been found in the solid state irrespective of the oxidation state of the chromophoric nucleus.

0108-2701/88/030489-07$03.00