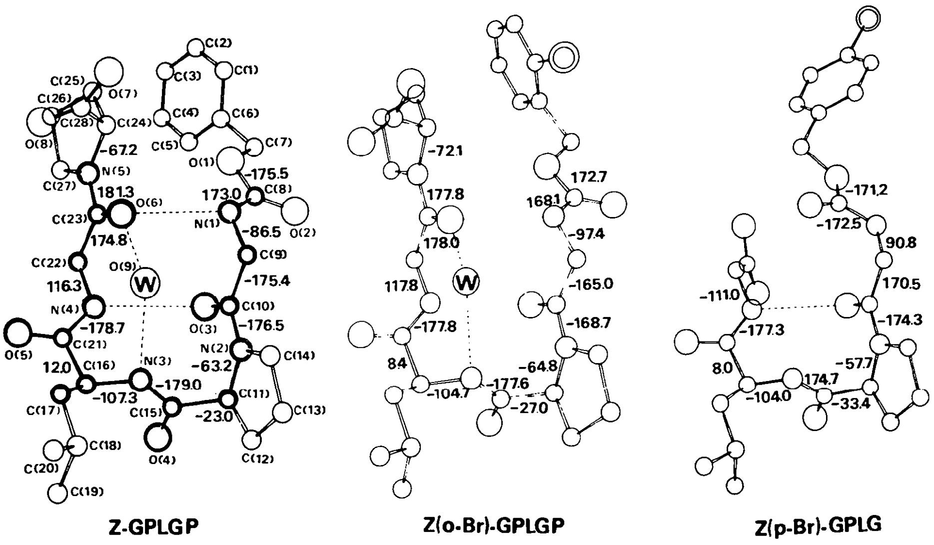

Z-GPLGP Z(o-Br)-GPLGP Z(p-Br)-GPLG

Fig. 3. Twisting angles (°) of the peptide chains. The convention is that defined by the IUPAC–IUB Commission on Biochemical Nomenclature (1970). The atoms linked by heavy bonds in Z-GPLGP are regarded as 'rigid' in the rigid-group search in the vector space. *W* represents an oxygen atom of the water molecule.

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1,2,3-Tris(2,4-dinitrophenoxy)benzene*

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Abstract. $C_{24}H_{12}N_6O_{15}$, m.p. 206 °C, triclinic, $P\bar{1}$, a = 10·453 (1), b = 16·524 (6), c = 8·146 (3) Å, α = 104·48 (3), β = 101·11 (2), γ = 71·28 (3)°, Z = 2, M_r = 624·38, D_c = 1·62 g cm^{-3}, for observed data R = 6·7%. The molecular conformation is *anti,anti* with the central dinitrophenoxy ring on the opposite side of the benzene ring from the outer two dinitrophenoxy rings, in agreement with PMR studies. In each phenoxy ring, the 2-nitro group is distal to the benzene ring. The 4-nitro groups are nearly coplanar with their rings while the 2-nitro groups deviate from coplanarity by about 40°. The diphenyl ether linkage of the central phenoxy ring is skewed (φ,φ': −68,−3°) while the outer phenoxy-ring conformations are twist-skewed (φ,φ': 65,33; −54,−32°).

Introduction. The crystal structure of the title compound (Fig. 1) was undertaken in order to study further the conformational preferences of highly hindered diaryl ethers (Lehmann, 1974), particularly those with

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* Conformations of Highly Hindered Aryl Ethers. XXVIII. Part XXVII: Lehmann (1973).

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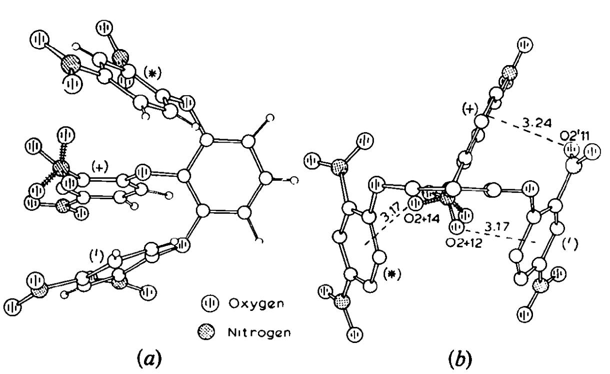
several equivalent moieties present in the same molecule. The results of PMR studies on simple 2,4-dinitrodiphenyl ethers suggest that they preferentially adopt a twist conformation with the rings rotated out of coplanarity with the C—O—C plane in opposite directions by approximately 37° (Lehmann, 1974). This conformation is the result of a balance between the conjugative tendency toward coplanarity with the ether bridge and the steric hindrance by the di-*ortho* substituents opposing coplanarity. However, in the case of the title compound, it was suggested by Lehmann (1974) that the central phenoxy ring adopted a skewed (one ring perpendicular to and the other coplanar with the central bridging plane) conformation with respect to the central benzene ring, in contrast to a twist conformation. In addition, this central dinitrophenoxy ring should be *anti* to both of the outer phenoxy rings.

Crystals of the title compound were synthesized and grown by recrystallization from acetone–ethanol (Lehmann, 1971). A crystal 0·16 × 0·24 × 0·24 mm was used to measure the lattice parameters and intensities. The cell constants were determined by least-squares analysis of the angular settings of 41 reflections having $2\theta > 50°$ [at 20°C; $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å]. The intensities of 3533 reflections (2580 reflections had $I > 2\sigma$) with $2\theta < 120°$ were measured on an Enraf–Nonius CAD-4 automated diffractometer. Reflections were measured in the θ–2θ scan mode using Ni-filtered Cu $K\alpha$ radiation and a sweep = $1{\cdot}2° + 0{\cdot}15° \tan(\theta)$. After the usual Lorentz and polarization corrections had been applied, normalized structure-factor amplitudes were computed and the structure was solved by application of direct methods with *MULTAN* (Germain, Main & Woolfson, 1971) and NQEST (De Titta, Edmonds, Langs & Hauptman, 1975). The complete structure was recognized from the first E map computed; this had an NQEST value of −0·66, the most negative value found among 64 ambiguities.

The atomic parameters were refined by full-matrix least-squares calculations. After three cycles of anisotropic refinement, an electron density difference map was computed which produced two large peaks in addition to the 12 H positions. The two extra peaks proved to be a $\frac{3}{4}$–$\frac{1}{4}$ disorder model of one of the nitro groups on the central dinitrophenoxy ring. The parameters for all atoms, excluding the H atoms, were refined for three final cycles. The weights used were the quantities $(1/\sigma_F^2)$, where σ_F is defined by Stout & Jensen (1968, equation H.14), and the instability correction was 0·06. This value increases σ_F for reflections with a large $|F|$ and prevents them from controlling the refinement. The R index, defined as $\sum\left||F_o| - |F_c|\right|/\sum |F_o|$, was 0·067 for the 2580 reflections used in the refinement, and 0·093 for all data. The weighted R $\{[\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}\}$ was 0·08. The function minimized in the least squares was $\sum w(|F_o| - |F_c|)^2$. The Fourier and least-squares programs are part of the Nonius crystallographic package for the PDP 11/45 computer. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final refined positional parameters are given in Table 1.*



(*a*) (*b*)

Fig. 1. Two views of the title compound illustrating its molecular conformation; in (*a*) the view is perpendicular to the plane of the phenoxy ring and in (*b*) end-on along the phenoxy plane.

Table 1. *Atomic coordinates for the title compound.*

The estimated standard deviations are listed in parentheses.

	x	y	z
C(1)	0.9123(3)	0.1269(2)	0.6093(4)
C(2)	0.7730(3)	0.1459(2)	0.6220(4)
C(3)	0.7328(3)	0.1039(2)	0.7178(5)
C(4)	0.8284(4)	0.0401(2)	0.7966(5)
C(5)	0.9626(4)	0.0216(2)	0.7790(5)
C(6)	1.0062(3)	0.0657(2)	0.6911(5)
O(11)	0.9518(2)	0.1680(1)	0.5082(3)
O(21)	0.6840(2)	0.2104(1)	0.5423(3)
O(31)	0.5946(2)	0.1179(1)	0.7285(4)
C(1')	0.5195(4)	0.2020(2)	0.7754(5)
C(2')	0.3811(3)	0.2263(2)	0.7074(5)
C(3')	0.3013(4)	0.3105(2)	0.7397(5)
C(4')	0.3593(4)	0.3711(2)	0.8485(6)
C(5')	0.4880(4)	0.3514(3)	0.9230(6)
C(6')	0.5715(4)	0.2657(3)	0.8863(6)
N(2'1)	0.3212(3)	0.1612(2)	0.5901(5)
O(2'11)	0.2372(3)	0.1843(2)	0.4716(5)
O(2'12)	0.3509(3)	0.0905(2)	0.6253(6)
N(4'11)	0.2735(4)	0.4631(2)	0.8785(5)
O(4'11)	0.1536(4)	0.4797(2)	0.8190(5)
O(4'12)	0.3247(4)	0.5179(2)	0.9659(8)
C(1*)	0.9273(3)	0.2556(2)	0.5570(5)
C(2*)	0.9020(4)	0.3042(2)	0.4332(5)
C(3*)	0.8824(5)	0.3925(2)	0.4739(5)
C(4*)	0.8800(4)	0.4327(2)	0.6414(5)
C(5*)	0.9054(4)	0.3882(2)	0.7697(5)
C(6*)	0.9302(3)	0.2984(2)	0.7265(4)
N(2*1)	0.8940(5)	0.2621(2)	0.2524(5)
O(2*11)	0.8325(6)	0.2062(3)	0.2042(6)
O(2*12)	0.9263(7)	0.2896(4)	0.1522(6)
N(4*1)	0.8549(5)	0.5279(2)	0.6862(5)
O(4*11)	0.8420(4)	0.5642(2)	0.8340(5)
O(4*12)	0.8385(6)	0.5663(2)	0.5746(6)
C(1+)	0.5911(3)	0.1897(2)	0.4109(4)
C(2+)	0.4973(3)	0.2582(2)	0.3429(4)
C(3+)	0.3972(3)	0.2440(2)	0.2140(5)
C(4+)	0.3891(3)	0.1602(2)	0.1530(4)
C(5+)	0.4816(4)	0.0896(2)	0.2114(5)
C(6+)	0.5831(3)	0.1050(2)	0.3425(5)
N(2+1)	0.5061(3)	0.3477(2)	0.4099(4)
O(2+11)	0.4904(7)	0.3904(3)	0.3101(7)
O(2+12)	0.5220(6)	0.3737(2)	0.5617(6)
O(2+13)	0.4141(14)	0.4029(9)	0.4719(27)
O(2+14)	0.6027(12)	0.3650(7)	0.3992(26)
N(4+1)	0.2799(3)	0.1437(2)	0.0177(4)
O(4+11)	0.2046(3)	0.2037(2)	−0.0436(4)
O(4+12)	0.2752(3)	0.0684(2)	−0.0300(4)

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* Lists of structure factors and thermal parameters, and a packing diagram have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33749 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. Fig. 1 shows that the overall conformation in the crystal is in general agreement with the PMR studies. The conformational parameters of this structure are listed in Table 2 and are compared with other dinitrophenoxy compounds in this series. The bond distances and angles calculated from the coordinates in Table 1 are shown in Fig. 2.

The conformation of this compound, as described by the torsion angles φ and φ' (Table 2), shows that the central phenoxy ring adopts a conformation nearer to skewed (φ,φ': $\pm 90,0°$), the proposed conformation, than twist-skewed (φ,φ': 90 ± 37, $0 \pm 37°$). However, the outer phenoxy rings adopt a twist-skewed conformation, analogous to that observed in thyroid hormone conformations (Cody, Hazel, Langs & Duax, 1977) rather than the proposed twist conformation (φ,φ': $\pm 37, > 37°$) proposed on the basis of PMR studies (Lehmann, 1974). The outer phenoxy rings are both twisted to position their 2-nitro groups away from the central phenoxy ring (Fig. 1).

In a similar study of bridging diphenyl ethers (van der Heijden, Griffith, Chandler & Robertson, 1975) both twist and skewed conformations were observed. Since all the structures listed in Table 2, as well as those reported by van der Heijden and his co-workers, belong to centrosymmetric space groups, the torsion angles for the diphenyl ether bridge will occur in the pairs φ and φ' of (+ +), (− −), or (+ −), (− +). Only the former sign combinations have been found in these studies (Table 2).

Table 2. *Conformational parameters for the title compound and related compounds*

Structure	φ	φ'	Reference‡
1,2,3-Tris(2,4-dinitrophenoxy)-benzene			(*a*)
(1)†	65°	33°	
(2)	−68	−3	
(3)	−54	−32	
2,4-Dinitronaphthyl 2′,6′-dimethylphenyl ether	60	22	(*b*)
2,4-Dinitro-6-bromophenyl 1′-naphthyl ether	68	25	(*c*)
2,4-Dinitrophenyl 2′,6′-diiodo-4′-methylphenyl ether	84	76	(*c*)

†	φ	φ'
(1)	C(2)–C(1)–O(11)–C(1*)	C(1)–O(11)–C(1*)–C(6+)
(2)	C(3)–C(2)–O(21)–C(1+)	C(2)–O(21)–C(1+)–C(6+)
(3)	C(2)–C(3)–O(31)–C(1′)	C(3)–O(31)–C(1′)–C(6′)

‡ References: (*a*) This work. (*b*) Cody *et al.* (1976). (*c*) Lehmann & Shefter (1972).

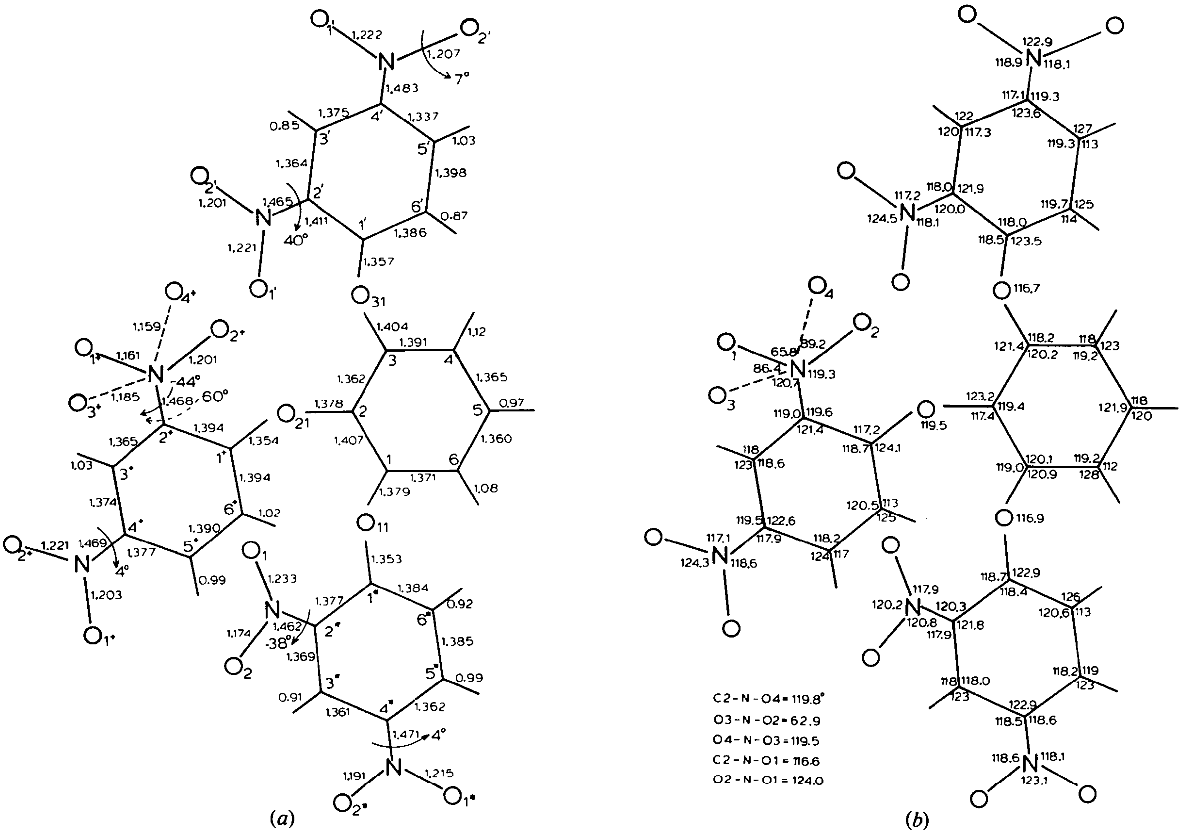

Fig. 2. (*a*) Bond distances (Å), nitro-group torsion angles (°) and numbering scheme and (*b*) bond angles (°) for the title compound. The e.s.d.'s for nonhydrogen bond lengths and angles are 0·005 Å and 0·4° respectively.

The *anti,anti* conformation established in this work provides ample justification for the assumptions which had to be made to interpret the PMR data for this and similar ethers studied previously (Lehmann, 1974). This in turn considerably strengthens the deductions made therein about the existence and approximate additivity of long-range anisotropic shielding effects.

All three 2-nitro groups are distal, *i.e.* directed away from the benzene ring. The deviations of the nitro groups from coplanarity with their respective phenoxy rings are shown in Fig. 2(*a*). These deviations are consistent with the patterns observed in the other 2,4-dinitroaryloxy structures (Table 2) (Cody, Shefter & Lehmann, 1976) where the 4-nitro group is nearly coplanar and the 2-nitro group has an average deviation of 40° from coplanarity with their respective phenoxy rings. These results are compatible with the observations made from an analysis of the factors affecting the conformation of aromatic nitro groups (Holden & Dickinson, 1977).

To determine whether there are any charge-transfer effects in this structure, as suggested by Lehmann (1974), the distances of the nitro O atoms to the centers of the phenoxy rings were computed. The closest intramolecular approaches† (Fig. 1*b*) were $C(X')\cdots O(2+12)$ (3·17 Å), $C(X^*)\cdots O(2+14)$ (3·17 Å) and $C(X+)\cdots O(2'11)$ (3·24 Å) and there was one close intermolecular contact: $O(2+13)\cdots O(4+12)$ (2·50 Å). This type of close contact also occurs in the other 2,4-dinitroaryloxy ethers listed in Table 2 (Cody *et al.*, 1976).

Since these interactions involve the O atoms of the disordered 2-nitro group of the central phenoxy ring, they perhaps provide enough stabilization energy to account for the disordering of this group. The skewed conformation of the central ring is therefore necessary to achieve this stabilization energy since this conformation places the O atoms of the disordered 2-nitro group equidistant from either outer phenoxy ring. Perhaps these interactions help maintain this twist-skewed conformation of the outer phenoxy rings.

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† These atom designations refer to the atom names as listed in Table 1.

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The Structure of 2,2′-Dinitroxydiethylnitramine (DINA)

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Abstract. $C_4H_8N_4O_8$, orthorhombic, $Pca2_1$, $a = 15\cdot345$ (5), $b = 6\cdot183$ (2), $c = 10\cdot095$ (3) Å, with $Z = 4$, $D_c = 1\cdot663$, $D_m = 1\cdot675$ g cm^{-3}. The structure has been solved from 1702 diffractometer-measured intensities to $R = 0\cdot043$. Both nitroxyethyl groups are planar to within 0·2 Å, the nitramine group is planar to within 0·13 Å. The shortest intermolecular contact is 2·90 Å between N and O of *b*-related molecules.

Introduction. The compound is one of a number of nitramines being investigated; interest lies in the possibility of intermolecular bonding in the structures. The