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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References

CODY, V., HAZEL, J. P., LANGS, D. A. & DUAX, W. L. (1977). *J. Med. Chem.* **20**, 1628–1631.
CODY, V., SHEFTER, E. & LEHMANN, P. A. (1976). *J. Cryst. Mol. Struct.* **6**, 223–233.
DE TITTA, G. T., EDMONDS, J. W., LANGS, D. A. & HAUPTMAN, H. A. (1975). *Acta Cryst.* A**31**, 472–479.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.
HEIJDEN, S. P. N. VAN DER, GRIFFITH, E. A., CHANDLER, W. D. & ROBERTSON, B. E. (1975). *Can. J. Chem.* **53**, 2084–2092.
HOLDEN, J. R. & DICKINSON, C. (1977). *J. Phys. Chem.* **81**, 1505–1514.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
LEHMANN, P. A. (1971). *Anal. Chim. Acta*, **54**, 321–336.
LEHMANN, P. A. (1973). *Rev. Soc. Quím. Mex.* **17**, 241–243.
LEHMANN, P. A. (1974). *Tetrahedron*, **30**, 719–726.
LEHMANN, P. A. & SHEFTER, E. (1972). *Rev. Latinoam. Quím.* **3**, 91–99.
STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*, p. 457. New York: Macmillan.

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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, $Pca2_1$, $a = 15{\cdot}345$ (5), $b = 6{\cdot}183$ (2), $c = 10{\cdot}095$ (3) Å, with $Z = 4$, $D_c = 1{\cdot}663$, $D_m = 1{\cdot}675$ g cm^{-3}. The structure has been solved from 1702 diffractometer-measured intensities to $R = 0{\cdot}043$. 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 title compound presents the possibility of both inter- and intramolecular bonding.

After failure to recrystallize the compound, crystals were selected from the original sample which was of unknown origin. Weissenberg photographs showed Laue symmetry *mmm* and gave the systematic absences: 0*kl*, *l* odd; *h*0*l*, *h* odd. The cell dimensions were measured from high-order θ values of *h*00, 0*k*0, and 00*l* with Cu $K\alpha$ radiation (λ = 1·5418 Å) on a diffractometer (Small & Travers, 1961). Intensities were collected on a Stoe STADI-2 automatic two-circle diffractometer using graphite-monochromatized Mo $K\alpha$ radiation (λ = 0·7107 Å) with crystals set on *b* and *c*; limiting 2θ was 70° on *b* and 75° on *c*. 2366 intensities were measured of which 664 with $I < 2\sigma(I)$ were omitted.

After allowance for changes in the standard reflexion, the data were scaled and merged using the *SHELX* suite of programs (Sheldrick, 1971) which was also used to obtain *E* values. Use of these in the program *MULTAN* (Germain, Main & Woolfson, 1971) gave the positions of the C, N and O atoms. Refinement of coordinates along with U_{ij} values was carried out using the program *CRYLSQ* of the XRAY 72 system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). At a later stage H-atom positions were obtained from difference Fourier maps and refined separately using U_{ij} values fixed equal to those of the atoms to which they were attached. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final value of *R* was 0·043; coordinates for non-hydrogen atoms are given in Table 1.*

Table 1. *Fractional atomic coordinates* (×10⁴) *for the* C, N *and* O *atoms*

	x	*y*	*z*
C(1)	6492 (2)	6350 (6)	4000 (fixed)
C(2)	5659 (2)	5624 (5)	3321 (5)
C(3)	5449 (2)	2121 (6)	2016 (5)
C(4)	6285 (2)	2130 (6)	1223 (4)
N(1)	8017 (2)	5903 (7)	3672 (5)
N(2)	5552 (1)	3261 (4)	3279 (4)
N(3)	5262 (2)	2291 (5)	4401 (4)
N(4)	7726 (2)	731 (7)	1368 (5)
O(1)	8579 (2)	5081 (7)	3001 (5)
O(2)	8084 (2)	6919 (7)	4675 (5)
O(3)	7186 (1)	5523 (5)	3167 (4)
O(4)	5208 (2)	3422 (5)	5396 (4)
O(5)	5094 (2)	347 (5)	4357 (4)
O(6)	6895 (1)	792 (5)	1950 (4)
O(7)	8231 (2)	9673 (7)	1995 (5)
O(8)	7828 (2)	1709 (6)	351 (5)

Table 2. *Bond distances* (Å) *involving the* C, N *and* O *atoms*

C(1)–C(2)	1·518 (4)	N(1)–O(1)	1·209 (6)
C(3)–C(4)	1·513 (5)	N(1)–O(2)	1·196 (7)
C(2)–N(2)	1·471 (4)	N(1)–O(3)	1·393 (4)
C(3)–N(2)	1·466 (6)	N(3)–O(4)	1·227 (6)
C(1)–O(3)	1·451 (4)	N(4)–O(7)	1·196 (6)
C(4)–O(6)	1·448 (5)	N(4)–O(8)	1·202 (7)
N(2)–N(3)	1·357 (5)	N(4)–O(6)	1·405 (4)
		N(3)–O(5)	1·230 (4)

Discussion. Bond distances and angles are given in Tables 2 and 3. Corresponding distances and angles in the two 'halves' of the molecule agree within the limits of experimental error. The terminal O–N–O angles of the nitroxy groups are appreciably larger than that in the nitramine part; the latter is in agreement with those found in other nitramines. Within one molecule, Fig. 1, the atoms lie in three planes; those of the nitramine group O(4)O(5)N(3)N(2)C(2)C(3) have a maximum deviation of 0·13 Å from their mean plane. Within the limits of error O(4)O(5)N(3)N(2) is planar with C(2) and C(3) displaced 0·154 and 0·302 Å. This feature is

Table 3. *Bond angles* (°) *involving the* C, N *and* O *atoms*

O(1)–N(1)–O(2)	129·4 (4)	O(7)–N(4)–O(8)	130·0 (4)
O(1)–N(1)–O(3)	112·1 (4)	O(7)–N(4)–O(6)	112·5 (4)
O(2)–N(1)–O(3)	118·5 (3)	O(6)–N(4)–O(8)	117·5 (3)
N(1)–O(3)–C(1)	113·6 (3)	N(4)–O(6)–C(4)	112·9 (3)
O(3)–C(1)–C(2)	104·6 (2)	O(6)–C(4)–C(3)	106·1 (3)
C(1)–C(2)–N(2)	113·6 (3)	C(4)–C(3)–N(2)	111·5 (3)
C(3)–N(2)–C(2)	121·0 (4)	N(2)–N(3)–O(4)	117·0 (3)
C(3)–N(2)–N(3)	118·5 (3)	N(2)–N(3)–O(5)	118·1 (4)
C(2)–N(2)–N(3)	116·9 (3)	O(4)–N(3)–O(5)	124·9 (4)

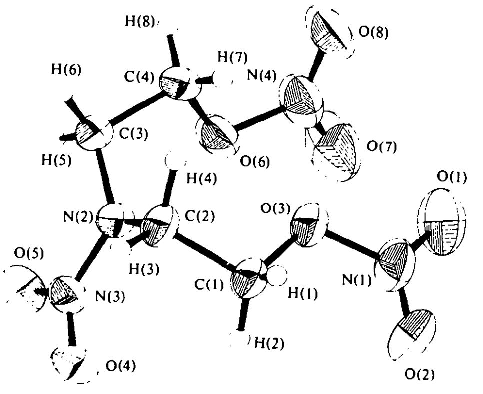

Fig. 1. Perspective view of the molecule, showing the numbering scheme.

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* Lists of structure factors, anisotropic thermal parameters and H-atom positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33765 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

common to all reported nitramine structures, the greatest deviation of C from the NNO_2 plane (0·536 Å) being found in cyclotrimethylene-trinitramine (Choi & Prince, 1972). In the present compound both nitroxyethyl groups are almost planar with only the amine C atoms C(3), C(2) appreciably deviating (0·118 and 0·187 Å). The intermolecular contact, 2·90 Å, between O(7) and N(1) of *b*-related molecules is less than the sum of the van der Waals radii (3·25 Å) across the π bonding electrons (Bondi, 1964); similar interactions, most probably polar in nature, have been found in other nitramine structures (Cobbledick & Small, 1973). An attempt was made to interpret the U_{ij} values in terms of rigid-body motion of the molecule, using the program *MGTLS* (Schomaker & Trueblood, 1968); the results suggested that the assumption of rigidity was likely to be invalid.

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References

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Choi, C. S. & Prince, E. (1972). *Acta Cryst.* B**28**, 2857–2862.

Cobbledick, R. E. & Small, R. W. H. (1973). *Acta Cryst.* B**29**, 1659–1666.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63–76.

Sheldrick, G. M. (1976). *SHELX* 76. Program for crystal structure determination. Univ. of Cambridge.

Small, R. W. H. & Travers, S. (1961). *J. Sci. Instrum.* **38**, 205–206.

Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. & Hall, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192, Computer Science Center, Univ. of Maryland, College Park, Maryland.

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The Structure of Erythromycin A Cyclic Carbonate

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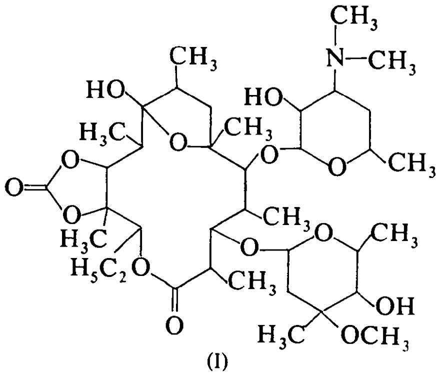
Abstract. $C_{38}H_{65}NO_{14}$, FW 759, $P2_12_12_1$, a = 17·08 (2), b = 22·02 (2), c = 10·84 (1) Å, Z = 4, V = 4075 Å^3, D_m = 1·23, D_c = 1·24 g cm^{-3}, $F(000)$ = 1648. 3117 reflections were measured on a Hilger & Watts automatic diffractometer with Mo $K\alpha$ radiation. The structure was refined by a full-matrix least-squares method to a final R index of 0·080. The structure appears to be in the 6,9-hemiacetal form and the absolute configuration at C(9) is R.

Introduction. The first successful attempt to obtain an erythromycin modification product of higher biological activity than that of the parent antibiotic gave erythromycin A cyclic carbonate (I) (Murphy, Stephens & Conine, 1968; Bojarska-Dahlig & Slawinski, 1972). As was stated earlier (Hempel, Bogucka-Ledochowska, Dauter, Borowski & Kosturkiewicz, 1975) the knowledge of the complete three-dimensional structure of the compound is particularly important when discussing the relation between molecular structure and biological activity and when formulating new derivatives. This analysis was undertaken to establish the absolute configuration at C(9) and also to confirm the position of the carbonate moiety. Some doubts were removed about the possible formation of 6,9-hemiacetal and 9-keto forms.



(I)

The sample of erythromycin carbonate was kindly supplied by Professor H. Bojarska-Dahlig from The Institute of Pharmaceutical Industry (Warsaw, Poland). Crystals were grown from methanol–ethyl acetate–water solution as colourless prisms elongated in the c direction. Dimensions of the crystal selected were 0·4 × 0·5 × 0·5 mm. Precession photographs

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