

Nature of the coordinated azide group

The presence of both anionic and coordinated azides in the crystal lattice permits a comparison of the bonding in the two forms. The present study has demonstrated that an azide group coordinated to a cobalt ion is distorted compared with an isolated symmetric azide anion. The distortion of the azide group is not as severe as if the azide were bonded to a carbon or hydrogen atom. In the case of coordination to a cobalt atom, the bond angle R-N-N is also increased. Crystal packing does not usually produce significant changes in the bond distances, therefore the asymmetry of the azide group is a direct consequence of the nature of the cobalt-azide bond.

A simple explanation for the above observations regarding distances and angles in the coordinated azide group is that resonance occurs between a state Co-N_3 and a second state Co^+N_3^- . Resonance between the two states results in a more symmetric azide with a larger bond angle R-N-N than in the case where the non-ionic form predominates in the ground state.

This study represents the first structure determination of a coordinated azide; thus there are no similar structures to which it can be compared. We are attempting to prepare the corresponding chromium salt for comparison with the cobalt salt. In addition samples of *m*- and *p*-azidonitrobenzene are available and will be studied in the future to investigate possible resonance of the azide group with the benzene ring.

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The Crystal and Molecular Structure of *cis*-1,2-Acenaphthenediol Dinitrate

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The crystal and molecular structure of *cis*-1,2-acenaphthenediol dinitrate has been determined by Patterson methods, and refined by ($F_o - F_c$) syntheses using partial three-dimensional data. The crystals are monoclinic with four molecules in a unit cell of dimensions

$$a = 17.10 \pm 0.02, \quad b = 4.242 \pm 0.005, \quad c = 19.18 \pm 0.02 \text{ \AA}; \quad \beta = 122^\circ 12' \pm 5',$$

the space group being $P2_1/c$.

The carbon skeleton is planar, with dimensions very similar to those found in other compounds containing the acenaphthene system. The C(1)-C(2) bond in the *peri*-ring has a length of 1.60 \AA which is significantly longer than a normal aliphatic single bond. There is no bonding between the nitroxy groups, which are planar and inclined at angles of $+62.1^\circ$ and $+71.2^\circ$ to the plane of carbon atoms. The average bond distances are: C-O, 1.47; O-N, 1.41; N=O, 1.19 \AA. All intermolecular contacts are normal.

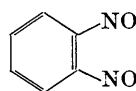
Introduction

Recently it has been demonstrated that *o*-dinitrosobenzene (I) has the benzofurazan-*N*-oxide (II) structure in the solid state (Hulme, 1962). A tautomeric form (III) in which the nitroxy groups are directly

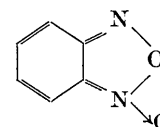
The author would like to thank Dr T. B. Joyner for his patience in obtaining suitable crystals. In addition the author wishes to thank the Data Computation Branch of the Test Department for running the author's IBM 709-7090 FORTRAN programs.

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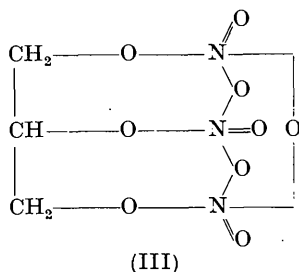
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(I)

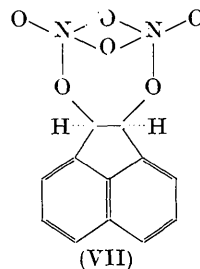
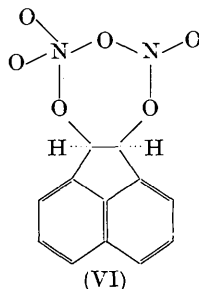
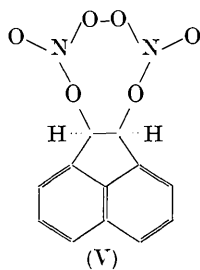
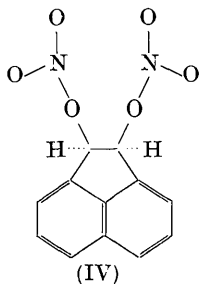


(II)



linked together has also been suggested for nitroglycerine to explain the mechanism of its polarographic reduction (Hetman, 1960). Furthermore, much evidence has been found for the steric interaction of contiguous nitroxy groups in cyclic and acyclic poly-nitrates (Csizmadia & Hayward, 1963). It therefore seems reasonable to speculate that ring formation is sometimes favoured in organic structures containing $-\text{NO}$, $-\text{NO}_2$ and $-\text{ONO}_2$ groups on suitably oriented carbon atoms.

Relatively little is known about the crystal and molecular structures of nitric esters. The only published X-ray work is that on pentaerythritol tetranitrate (Booth & Llewellyn, 1947; Trotter, 1963) in which no bonding between nitroxy groups was found. However, the compound is almost unique among nitric esters, and can hardly be regarded as a typical example.



cis-1,2-Acenaphthenediol dinitrate (IV), first synthesized by Csizmadia & Hayward (1963), provides a rigorous test of the possibility of intramolecular bonding between nitroxy groups. In structures V and VI the stereochemical configurations can be easily assumed by rotation about single bonds, and the non-planar eight- and seven-membered rings thus formed are completely free of strain. A strained structure

(VII) would be analogous to one proposed for dinitrogen tetroxide (Gray, 1958). To decide between these structures, an X-ray investigation of the crystalline material was carried out.

Experimental

Crystals of *cis*-acenaphthenediol dinitrate are colourless needles elongated along the *b* axis with the (001) face well developed. The density was measured by flotation in aqueous potassium iodide. The cell constants and space group were determined from rotation and oscillation photographs of a crystal rotating about the *b* axis, *h*0*l* and *h*1*l* Weissenberg films, and 0*kl* and *hk*0 precession films.

Crystal data

cis-Acenaphthenediol dinitrate, $\text{C}_{10}\text{H}_6(\text{CHONO}_2)_2$;
 $M = 276.20$; m.p. 128.0–130.5 °C.

Monoclinic,

$$a = 17.10 \pm 0.02, \quad b = 4.242 \pm 0.005, \\ c = 19.18 \pm 0.02 \text{ \AA}; \quad \beta = 122^\circ 12' \pm 5'.$$

Volume of the unit cell: 1177.3 Å³.

Density: calculated (with $Z = 4$) = 1.557, measured = 1.53 g.cm⁻³.

Absorption coefficients for X-rays:

$$\lambda = 1.5418 \text{ \AA}, \quad \mu = 12.70 \text{ cm}^{-1}; \\ \lambda = 0.7107 \text{ \AA}, \quad \mu = 1.57 \text{ cm}^{-1}.$$

Total number of electrons per unit cell: $F(000) = 568$.

Absent spectra: *h*0*l* when *l* is odd, 0*k*0 when *k* is odd. Space group is $P2_1/c$ (C_{2h}^2).

For the collection of intensity data a needle crystal of cross-section 0.07 × 0.11 mm was mounted about the *b* axis. Equi-inclination Weissenberg photographs of the *h*0*l* and *h*1*l* layers were taken with Cu $K\alpha$ radiation. To extend the intensity range the data for each zone were collected on two sets of four films related by time exposures. The intensities of the various reflexions were estimated visually and corrected as usual for Lorentz and polarization factors. No absorption corrections were considered necessary. 246 *h*0*l* (excluding the 100 and $\bar{1}02$ reflexions which were cut off by the beam trap) and 443 *h*1*l* independent reflexions were found to be of measurable magnitude; these represent 75% and 76%, respectively, of the total number theoretically observable.

Structure analysis

The first attempts to derive an approximate structure made use of the set of *h*0*l* data. A Patterson synthesis projected down the short *b* axis (Fig. 1) was computed. The highest peaks on this map were readily identified as multiple vector peaks between naphthalene rings related by symmetry, leading to a position of $x = 0.258$, $z = 0.196$ or $x = 0.242$, $z = 0.304$ for the molecular origin, defined as the centre of the C(5a)–C(8b) bond. The

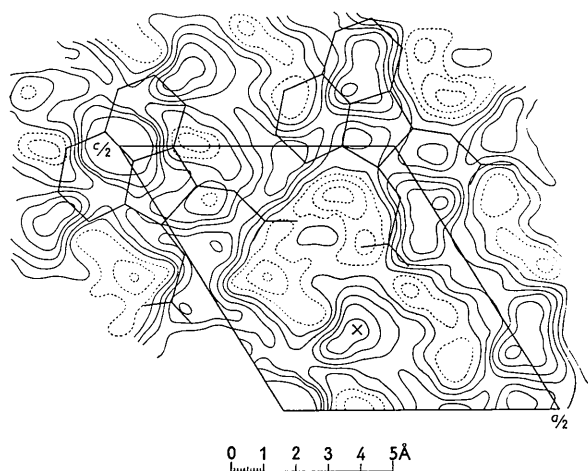


Fig. 1. Patterson projection on (010). Contour-line scale arbitrary. A diagram of two molecules is superimposed. The multiple vector peak between nitroxy groups is marked with a cross.

orientation of the aromatic nucleus indicated by the Patterson map was in agreement with that deduced from an examination of the weighted reciprocal lattice. The extended peak marked with a cross (about 3.4 Å from the origin) could be reasonably ascribed to interactions between non-bonded nitroxy groups. On this basis structure (IV), with its many conformations involving rotations about C-O and O-N single bonds, was taken as a starting point for the precise location of atoms by Fourier methods.

[010] Projection

The shortness of the b axis promised a good view of the structure in this projection. The x and z coordinates of the carbon atoms were obtained from the projection of a CENCO Petersen molecular model held in the deduced orientation, the molecular origin being arbitrarily placed at $x=0.258$, $z=0.196$. Vari-

ous sets of x and z parameters were postulated for the oxygen and nitrogen atoms, allowing for the fact that the two nitroxy groups must be approximately 3.4 Å apart, and oriented in such a way that the 'thickness' of the molecule in the [010] direction was not excessive. The different trial structures were tested by calculating $h0l$ structure amplitudes and comparing them with the observed values. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962), and an overall isotropic temperature factor $B=4.5 \text{ \AA}^2$ was used. Finally a structure which gave reasonable agreement with the low-order reflexions was chosen for refinement. The discrepancy index R (observed reflexions only) was 0.618, a rather high value, but it was possible to allocate signs to 155 observed reflexions for a Fourier synthesis. All the

Table 1. *Final parameters**

Atom	x	y	z	B (\AA^2)	Δ (\AA)
C(1)	0.3234	0.455	0.2289	4.3	-0.003
C(2)	0.2187	0.387	0.1564	4.3	+0.038
C(2a)	0.1746	0.193	0.1941	4.4	-0.034
C(3)	0.0871	0.080	0.1617	5.0	+0.008
C(4)	0.0681	-0.081	0.2181	5.8	-0.002
C(5)	0.1336	-0.116	0.3015	5.6	-0.023
C(5a)	0.2230	0.024	0.3341	5.2	+0.020
C(6)	0.2943	0.008	0.4172	5.4	+0.019
C(7)	0.3780	0.140	0.4400	4.9	+0.005
C(8)	0.3982	0.306	0.3852	4.9	+0.035
C(8a)	0.3268	0.298	0.3019	4.7	-0.053
C(8b)	0.2409	0.171	0.2786	4.8	-0.006
O(1)	0.3882	0.273	0.2168	4.6	+0.007
N	0.4070	0.398	0.1592	4.9	-0.030
O(2)	0.3660	0.631	0.1230	6.1	+0.010
O(3)	0.4675	0.262	0.1605	5.7	+0.011
O(1')	0.2216	0.191	0.0947	5.0	-0.015
N'	0.1530	0.257	0.0120	5.2	+0.058
O(2')	0.0915	0.424	0.0009	7.2	-0.025
O(3')	0.1636	0.082	-0.0333	6.8	-0.021

* The numbering of the carbon atoms (see Fig. 3) follows the rules recommended in the *I.U.P.A.C. 1957 Rules* (1958).

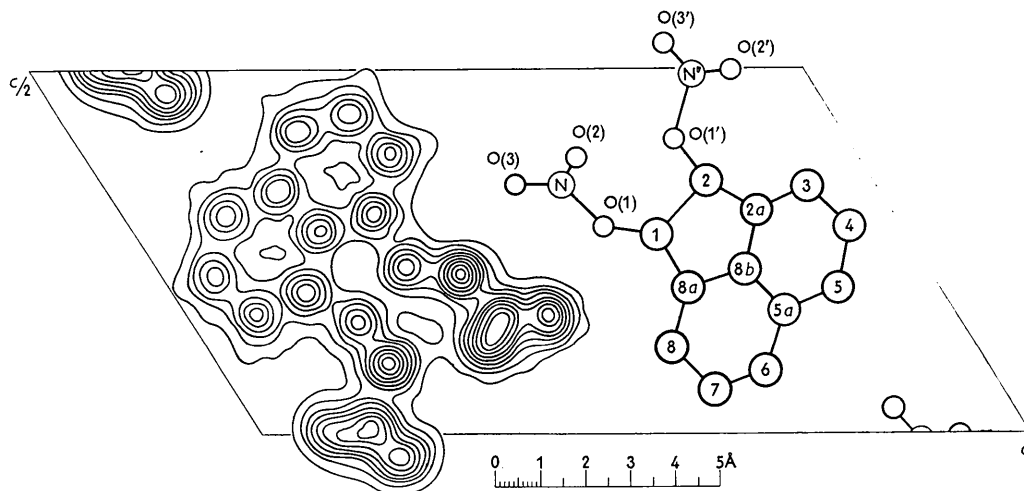


Fig. 2. Electron-density projection on (010). Contour lines are drawn at intervals of $1 \text{ e.}\text{\AA}^{-2}$ starting with $1 \text{ e.}\text{\AA}^{-2}$.

atoms could be identified, and there were no spurious details in the electron-density map. However, further refinement proved less encouraging and R could not be improved below about 0.40. This suggested that the molecule had essentially the correct structure and orientation, but was wrongly placed in the unit cell. New x and z coordinates for all the atoms were now deduced with the molecular origin shifted to the alternative position $x=0.242$, $z=0.304$. Recalculation of the $h0l$ structure factors gave an R value of 0.523 and in five cycles of refinement by difference synthesis this was reduced to 0.160. The final electron-density projection on (010) is shown in Fig. 2.

y Parameters and final refinement

The y coordinates of the atoms were derived from the $h1l$ data. Approximate y parameters referred to the molecular origin were derived from a molecular model, and the y coordinate of the molecular origin was chosen as that which gave the best agreement between the calculated and observed structure factors for a few low-order data. Structure factors were now calculated for all $h1l$ reflexions, using the y parameters thus determined and the x , z and B parameters from the $h0l$ refinement. The initial value of R for the observed reflexions was 0.347. Refinement of all the positional and temperature parameters proceeded by

Table 3 (cont.)

h	ℓ	E_o	E_c	h	ℓ	E_o	E_c	h	ℓ	E_o	E_c	h	ℓ	E_o	E_c
-12	12	2.9	-1.3	8 13	3.8	3.7	0.15	1.9	-0.9	1 17	<1.3	-1.1			
-11	12	1.8	0.3	-20 14	<1.0	-1.3	1 15	2.1	-5.9	2 17	<1.2	3.2			
-10	12	13.9	13.5	-19 14	4.3	-4.9	2 15	<1.5	-4.5	3 17	2.2	-0.8			
-9	12	5.4	7.6	-18 14	2.3	-4.3	3 15	2.8	1.8	4 17	1.5	2.7			
-8	12	23.0	-26.5	-17 14	2.5	6.2	4 15	3.2	0.6	5 17	1.3	1.8			
-7	12	3.2	2.5	-16 14	8.4	11.5	5 15	1.6	0.2	-20 28	2.7	-3.9			
-6	12	5.4	-8.6	-15 14	8.4	-8.1	6 15	<1.0	1.7	-19 18	2.5	-3.7			
-5	12	6.6	9.1	-14 14	5.3	5.0	-20 16	<1.0	-2.4	-18 18	<1.2	1.3			
-4	12	5.8	-8.3	-13 14	8.4	-10.2	-19 16	4.3	2.4	-17 18	<1.3	0.7			
-3	12	21.1	19.6	-12 14	2.3	3.5	-18 16	<1.3	-1.7	-16 18	<1.3	1.6			
-2	12	20.6	22.8	-11 14	8.8	9.6	-17 16	<1.4	2.2	-15 18	<1.4	0.4			
-1	12	7.6	-9.8	-10 14	6.9	-6.9	-16 16	<1.4	0.8	-14 18	<1.4	2.0			
0	12	2.0	-1.3	-9 14	<1.4	0.1	-15 16	<1.5	-1.1	-13 18	4.2	4.7			
1	12	14.4	-15.7	-8 14	5.3	-4.4	-14 16	5.0	-4.5	-12 18	16.9	-15.6			
2	12	<1.5	-0.9	-7 14	<1.4	2.4	-13 16	<1.5	-0.4	-11 18	7.7	7.4			
3	12	6.1	6.0	-6 14	2.5	4.5	-12 16	8.2	9.7	-10 18	2.6	4.6			
4	12	<1.5	-0.8	-5 14	10.3	-8.7	-11 16	6.1	-6.9	-9 18	6.5	5.8			
5	12	6.4	-5.3	-4 14	8.5	7.8	-10 16	<1.5	-2.5	-8 18	6.1	6.0			
6	12	<1.4	1.2	-3 14	2.5	-2.1	-9 16	<1.5	2.7	-7 18	25.1	-19.1			
7	12	<1.3	0.5	-2 14	2.3	-7.0	-8 16	<1.5	1.8	-6 18	2.3	-5.0			
8	12	2.4	2.6	-1 14	13.9	16.0	-7 16	2.6	2.3	-5 18	8.7	10.6			
9	12	<1.0	-0.0	0 14	22.2	-17.5	-6 16	7.8	-5.6	-4 18	<1.5	-2.8			
-19	13	<1.2	-0.8	1 14	5.3	6.0	-5 16	13.1	-15.5	-3 18	7.9	6.1			
-18	13	6.7	-6.3	2 14	3.1	3.3	-4 16	14.1	14.3	-2 18	4.9	-3.8			
-17	13	5.8	-3.7	3 14	2.1	-4.2	-3 16	11.2	7.8	-1 18	<1.3	-0.8			
-16	13	<1.5	5.6	4 14	2.0	2.4	-2 16	2.7	5.4	0 18	2.5	4.6			
-15	13	<1.5	6.2	5 14	1.9	-0.8	-1 16	10.3	-9.3	1 18	4.9	-5.0			
-14	13	9.3	11.0	6 14	<1.2	-0.1	0 16	<1.5	-3.3	2 18	2.9	2.8			
-13	13	6.4	-8.6	7 14	3.2	4.3	-20 17	3.5	3.9	3 18	2.3	-2.3			
-12	13	<1.5	-5.8	-20 15	2.1	-2.5	-19 17	4.4	-3.1	-18 19	1.9	-2.1			
-11	13	17.7	15.5	-19 15	<1.2	-0.6	-18 17	<1.2	-1.1	-14 19	4.0	3.3			
-10	13	2.2	-5.1	-18 15	7.6	6.4	-17 17	<1.3	1.6	-8 19	6.3	-5.7			
-9	13	4.7	-4.7	-17 15	4.5	5.3	-16 17	<1.4	-0.8	-6 19	3.6	4.7			
-8	13	<1.4	-0.0	-16 15	4.7	-3.1	-15 17	<1.5	1.6	-5 19	3.5	-2.7			
-7	13	1.9	-3.6	-15 15	2.4	5.8	-14 17	<1.5	-1.6	-3 19	3.6	3.2			
-6	13	<1.4	0.2	-14 15	<1.5	-0.7	-13 17	<1.5	-1.1	-2 19	3.1	2.8			
-5	13	1.9	-3.3	-13 15	5.3	-6.7	-12 17	4.9	-6.0	-1 19	1.7	-0.0			
-4	13	<1.4	0.3	-12 15	3.1	1.9	-11 17	<1.5	0.6	-13 20	2.7	-3.0			
-3	13	5.6	-7.1	-11 15	11.7	-15.4	-10 17	5.5	5.7	-8 20	4.4	-3.9			
-2	13	7.8	9.8	-10 15	<1.5	-4.4	-9 17	2.2	-3.5	-17 21	3.1	3.8			
-1	13	3.6	6.7	-9 15	5.1	7.6	-8 17	11.9	10.5	-15 21	4.3	-4.7			
0	13	20.0	-16.6	-8 15	5.7	-7.2	-7 17	11.9	11.1	-14 21	2.4	2.0			
1	13	<1.5	2.3	-7 15	<1.5	-0.6	-6 17	11.9	-6.7	-11 21	5.1	-4.0			
2	13	6.9	9.7	-6 15	2.1	0.9	-5 17	7.9	-5.9	-9 21	5.1	3.5			
3	13	3.1	3.5	-5 15	6.0	9.6	-4 17	2.2	-0.5	-13 22	3.2	-2.8			
4	13	2.1	-2.7	-4 15	13.8	17.9	-3 17	<1.5	-0.9	-10 22	7.9	5.6			
5	13	<1.4	-3.0	-3 15	2.1	3.7	-2 17	2.1	-2.7	-7 22	1.5	-1.4			
6	13	<1.3	-0.6	-2 15	2.2	-4.1	-1 17	<1.4	0.6	-9 23	1.6	1.8			
7	13	<1.2	-0.9	-1 15	3.1	-4.5	0 17	4.4	-3.5	-7 23	2.0	-1.9			

computing cosine and sine difference generalized projections (Rossmann & Shearer, 1958), and after five cycles R dropped to 0.169. The observed values for the very intense $\bar{2}11$, $\bar{3}12$, $\bar{2}12$, $\bar{3}13$, $\bar{2}13$ reflexions were considerably larger than F_c , probably owing to errors in intensity estimation, and these planes were omitted in evaluating R .

Structure factors were again calculated for the $h0l$ reflexions with the parameters determined from the $h1l$ refinement, the R value being reduced slightly from 0.160 to 0.145. Measured and calculated $h0l$ and $h1l$ structure factors are listed in Tables 2 and 3 respectively.

Coordinates, molecular dimensions, and orientations

The final positional and temperature parameters are given in Table 1, where the atomic coordinates are expressed as fractions of the unit-cell edges.

The dimensions of the molecule, calculated from these coordinates, are shown in Table 4. Mean bond

Table 4. Bond lengths, valency angles and some intramolecular approach distances

(a) Bond lengths			
C(5a)-C(8b)	1.40 Å	C(1)-C(2)	1.60 Å
C(8b)-C(2a)	1.40	C(2)-C(2a)	1.53
C(8b)-C(8a)	1.40	C(1)-C(8a)	1.52
C(2a)-C(3)	1.37	C(2)-O(1')	1.47
C(8a)-C(8)	1.40	C(1)-O(1)	1.47
C(3)-C(4)	1.46	O(1')-N'	1.41
C(8)-C(7)	1.45	O(1)-N	1.41
C(4)-C(5)	1.39	N'-O(2')	1.19
C(7)-C(6)	1.37	N-O(2)	1.20
C(5)-C(5a)	1.44	N'-O(3')	1.23
C(6)-C(5a)	1.40	N-O(3)	1.17
(b) Valency angles			
C(1)-C(2)-C(2a)	107°	C(7)-C(8)-C(8a)	115°
C(2)-C(2a)-C(8b)	107	C(8)-C(8a)-C(8b)	120
C(2a)-C(8b)-C(8a)	114	O(1')-C(2)-C(1)	107
C(8b)-C(8a)-C(1)	111	O(1')-C(2)-C(2a)	108
C(8a)-C(1)-C(2)	101	C(2)-O(1')-N'	115
C(2a)-C(3)-C(4)	117	O(1')-N'-O(2')	117
C(3)-C(4)-C(5)	123	O(1')-N'-O(3')	109
C(4)-C(5)-C(5a)	118	O(2')-N'-O(3')	133
C(5)-C(5a)-C(8b)	118	O(1)-C(1)-C(2)	111
C(5a)-C(8b)-C(2a)	123	O(1)-C(1)-C(8a)	105
C(8b)-C(2a)-C(3)	121	C(1)-O(1)-N	116
C(8a)-C(8b)-C(5a)	123	O(1)-N-O(2)	117
C(8b)-C(5a)-C(6)	118	O(1)-N-O(3)	112
C(5a)-C(6)-C(7)	118	O(2)-N-O(3)	131
C(6)-C(7)-C(8)	125		
(c) Selected intramolecular distances			
O(1)-O(1')	2.57 Å	C(2)-N'	2.43 Å
O(1')-C(2a)	2.43	C(2)-O(2')	2.60
O(1')-C(1)	2.48	C(1)-N	2.43
O(1)-C(8a)	2.37	C(1)-O(2)	2.61
O(1)-C(2)	2.53	O(1')-O(2)	2.91

lengths and valency angles were obtained by assuming symmetry m for the *cis*-acenaphthenediol portion of the molecule (Fig. 3), and by averaging correspond-

ing values for the two nitroxy groups (Fig. 4(a)). The equations of the mean planes are

Carbon atoms:

$$-0.470X' + 0.866Y + 0.172Z' - 0.813 = 0,$$

Unprimed ONO₂:

$$0.358X' + 0.591Y + 0.723Z' - 4.805 = 0,$$

Primed ONO₂:

$$0.664X' + 0.745Y - 0.062Z' - 2.397 = 0,$$

where X' , Y , Z' are coordinates expressed in Å and referred to orthogonal axes a , b and c' . The deviations of the atoms from these planes are listed in the last column of Table 1. The unprimed and primed ONO₂ groups (Fig. 2) are inclined to the plane of carbon atoms at angles of $+62.1^\circ$ and $+71.2^\circ$ respectively.

The orientation of the molecule in the crystal may be indicated by giving the angles χ , ψ and ω (Table 5),

Table 5. *Molecular orientation in the crystal*

$\chi_L = 128.9^\circ$	$\chi_M = 51.5^\circ$	$\chi_N = 118.0^\circ$
$\psi_L = 101.4$	$\psi_M = 62.5$	$\psi_N = 30.0$
$\omega_L = 138.7$	$\omega_M = 129.1$	$\omega_N = 80.1$

which the molecular axes L , M (Fig. 3) and the carbon-plane normal N make with the a and b crystal axes, and their perpendicular c' . The axis L was taken through the mid-points of bonds C(3)–C(4) and C(7)–C(8), and axis M through C(5a) and the centre of the C(1)–C(2) bond. L , M and N are thus not exactly mutually orthogonal, the angles being $\angle LM = 90.6^\circ$, $\angle LN = 90.2^\circ$, and $\angle MN = 90.0^\circ$.

Standard deviations

The standard deviations of the x and z coordi-

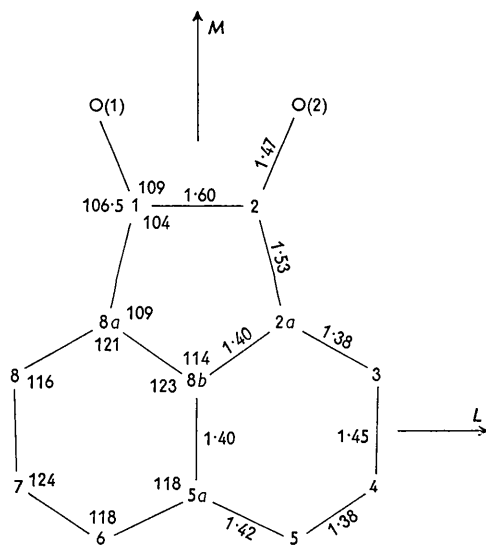


Fig. 3. Numbering and average dimensions of the *cis*-acenaphthenediol portion of the molecule.

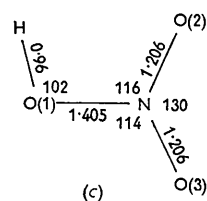
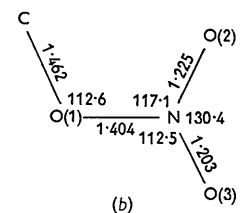
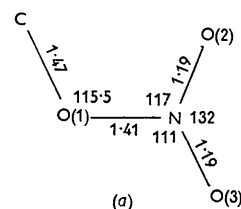


Fig. 4. Dimensions of the nitroxy group in (a) *cis*-1,2-acenaphthenediol dinitrate, (b) pentaerythritol tetranitrate, and (c) nitric acid.

nates, calculated by Cruickshank's (1949) formulae, are $\sigma(x) = \sigma(z) = 0.010$ Å for C, 0.008 Å for O(1), 0.009 Å for N, and 0.010 Å for O(2) and O(3). $\sigma(y)$ is expected to be somewhat greater, but since most of the bonds are inclined at quite small angles to (010), the standard deviations of the measured bond distances are about 0.014 Å for C–C and N=O bonds, 0.013 Å for C–O and 0.012 for O–N bonds. All valency angles have a standard deviation of approximately 0.9° .

Intermolecular distances

All the intermolecular distances correspond to normal van der Waals interactions. Packing of the molecules in the unit cell and some shorter lateral intermolecular contacts are shown in Fig. 5.

Discussion

The y coordinates have not been determined to a high degree of accuracy, so that the apparently significant deviations from the mean planes of the acenaphthene nucleus (maximum value 0.053 for C(8a)) and of the nitroxy groups (maximum value 0.058 for N') are probably not significant. Since the b axis is short, small errors in the y parameters should not seriously affect the measured bond lengths and valency angles.

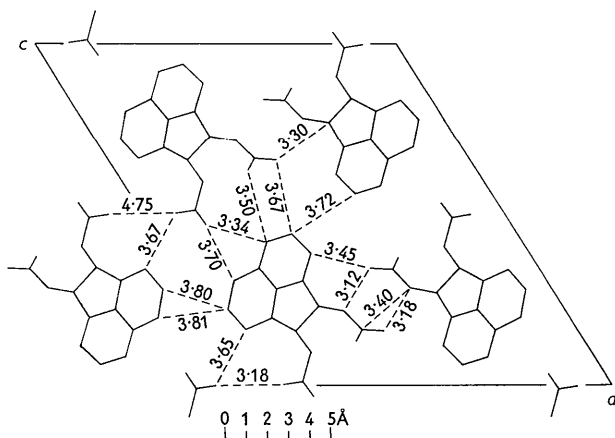


Fig. 5. Projection of the structure on (010), showing the shorter intermolecular distances.

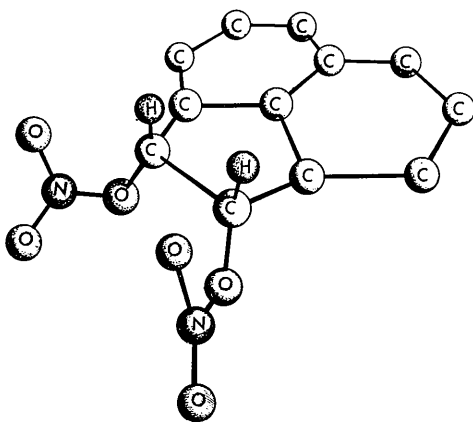


Fig. 6. Perspective diagram of the molecular structure of *cis*-acenaphthenediol dinitrate. The two planar nitroxy groups are inclined to the plane of carbon atoms in the same sense.

The molecular structure of *cis*-1,2-acenaphthenediol dinitrate is shown in perspective in Fig. 6. The nitroxy groups are well separated from each other, the two shortest contacts between them being $O(1)-O(1') = 2.57 \text{ \AA}$ and $O(1')-O(2) = 2.91 \text{ \AA}$. The planes of the nitroxy groups are inclined in the same sense with respect to the plane of carbon atoms.

The dimensions of the acenaphthene nucleus of *cis*-1,2-acenaphthenediol dinitrate are very similar to those found in other acenaphthene derivatives. The strain in the *peri*-ring is almost entirely taken up in valency-angle distortions, both in the *peri*-ring and in the naphthalene rings. The lengths of bonds $C(2a)-C(3)$, $C(3)-C(4)$, $C(4)-C(5)$ vary in the order short-long-short, as do the corresponding distances in naphthalene.

The aliphatic $C(1)-C(2)$ bond has a length of $1.60_3 \pm 0.01_4 \text{ \AA}$ (projection on (010) 1.57_8 \AA), which agrees well with the value $1.59_6 \pm 0.01_4 \text{ \AA}$ reported for *cis*-1,2-acenaphthenediol (Trotter & Mak, 1963). The significant lengthening of this bond, as compared with the values 1.54 \AA and 1.53 \AA found in acenaphthene (Ehrlich, 1957) and acenaphthenequinone (Mak & Trotter, 1963) respectively, may be ascribed to steric repulsion of the non-bonded oxygen atoms $O(1)$ and $O(1')$.

The bond lengths and valency angles of the nitroxy group found in the present study are compared with those of pentaerythritol tetranitrate (Trotter, 1963) and nitric acid (Millen & Morton, 1960) in Fig. 4. There is excellent agreement among corresponding values, and in both nitrates $\angle O(1)NO(2)$ is significantly greater than $\angle O(1)NO(3)$ as a consequence of steric interference between atoms C and $O(2)$.

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