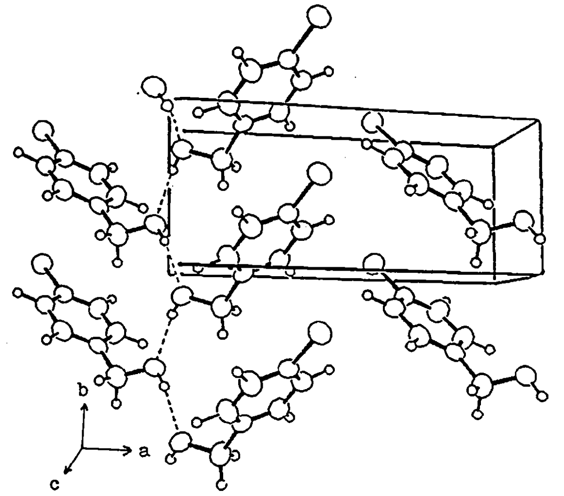

Fig. 2. An *ORTEP* drawing of the crystal structure viewed along the *c* axis. Broken lines denote hydrogen bonds.

The molecular packing projected along the *c* axis is illustrated in Fig. 2. The crystal structure of the compound is characterized by chains of O—H···O hydrogen bonds running along a 2_1 axis. The O···O distance of 2·746 (4) Å is within the usual range, although it is longer than the 2·66 Å found in methanol having similar hydrogen-bond chains (Tauer & Lipscomb, 1952). The molecules linked by the hydrogen-bond chains are held together by van der Waals interactions. The shortest intermolecular distance between Cl atoms is 3·641 (2) Å; Cl···H(71) (2·98 Å) is slightly less than the van der Waals contact. The Cl atom of a molecule is placed just above the benzene ring of the adjacent molecule related by a *b* translation. However, the distance between the Cl atom and the mean plane of the benzene ring [3·694 (2) Å] is longer than the normal van der Waals contact, indicating the absence of specific interactions between them.

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Structure of 4-Chloro-7-nitro-2,1,3-benzoxadiazole

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Abstract. $C_6H_2ClN_3O_3$, $M_r = 199·55$, monoclinic, $P2_1$, $a = 13·420\ (1)$, $b = 5·410\ (2)$, $c = 10·703\ (1)$ Å, $\beta = 102·36\ (1)°$, $V = 759·0\ (3)$ Å^3, $Z = 4$, D_m not measured, $D_x = 1·746$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0·71069$ Å, $\mu = 4·7$ mm^{-1}, $F(000) = 400$, $T = 296$ K, final $R = 0·048$ for 1484 observed reflections. The two independent molecules of the asymmetric unit have different structures, resulting from different packing environments. There is a distinct double-bond fixation in the six-membered ring of the molecule. The non-centrosymmetric crystal structure is consistent with the observation of second-harmonic generation.

Introduction. The structure of 2,1,3-benzoxadiazole (BFZ) has been of particular interest concerning the double-bond fixation in the six-membered ring. It has been shown that BFZ is more aromatic than the sulfur (BTD) and selenium (BSD) analogues which exhibit considerable quinoid character in the six-membered ring in crystals (Luzzati, 1951). Microwave study has,

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to the contrary, indicated a structure for BFZ displaying double-bond fixation in the six-membered ring (Brown, Lister & Tyler, 1970). Our recent study has revealed that the title compound (NBD-Cl) generates phase-matched second-harmonic radiation when exposed to the 1·06 µm output of an Nd-YAG laser. Because nonlinear optical processes are of both intramolecular and crystalline nature it is important to know the crystal structure of nonlinear optical materials (Williams, 1983). The structure of NBD-Cl was thus required for the understanding of its nonlinear optical properties.

Experimental. Material obtained from DOJINDO Laboratories was crystallized from acetone and dissolved to appropriate size in diethyl ether. A pale-yellow ellipsoidal single crystal of dimensions 0·76 × 0·55 × 0·48 mm was used for data collection. Preliminary survey was made with Weissenberg photographs. The X-ray measurements were carried out on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Unit-cell parameters were determined by a least-squares fit of 2θ values for 25 reflections in the range $9 < \theta < 13°$. Intensities up to $2\theta = 50°$ for $h = -15$ to 15, $k = 0$ to 6, $l = 0$ to 12 were measured by ω–2θ scans for $\Delta\omega = (0{\cdot}65 + 0{\cdot}35\tan\theta)°$ plus 50% for the background. Of the 1566 reflections measured, 1484 were observed with $I > 3{\cdot}0\sigma(I)$. Three standard reflections every hour of radiation time varied within 2%; no intensity correction was made. No correction for absorption.

The structure was solved by direct methods (*MULTAN*82: Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and refined by full-matrix least squares with anisotropic temperature factors for non-H atoms and isotropic ones for H. H atoms were located from a difference Fourier synthesis. Maximum (Δ/σ) ratio in final cycle was 0·41. Quantity minimized was $\sum w(F_o - F_c)^2$, $w = 1/\sigma^2(F)$. The final R (wR) and S values were 0·048 (0·050) and 0·73. The final difference Fourier map showed no peaks above 0·37 e Å^{-3}. Scattering factors for the non-H atoms were taken from *International Tables for X-ray Crystallography* (1974), those for H from Stewart, Davidson & Simpson (1965). All calculations were performed by the CAD-4 *SDP* system (Frenz, 1978) and diagrams were drawn with *ORTEP*II (Johnson, 1976).

Discussion. Atomic parameters and geometrical data are given in Tables 1* and 2, respectively. Fig. 1 shows

Table 1. *Final positional and equivalent isotropic temperature parameters* $\{B_{eq} = \frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]\}$ *for non-*H *atoms with e.s.d.'s in parentheses*

	x	y	z	B_{eq}(Å^2)
Molecule (I)				
Cl	0·1630 (1)	0·063	0·6572 (2)	5·07 (3)
O(1)	−0·1754 (3)	0·125 (1)	0·5557 (4)	5·2 (1)
O(2)	−0·2275 (3)	0·741 (1)	0·7619 (5)	5·9 (1)
O(3)	−0·1026 (4)	0·993 (1)	0·8875 (5)	6·7 (1)
N(1)	−0·1928 (4)	0·327 (1)	0·6276 (5)	4·3 (1)
N(2)	−0·0734 (4)	0·071 (1)	0·5705 (5)	4·5 (1)
N(3)	−0·1367 (4)	0·770 (1)	0·8115 (5)	4·5 (1)
C(1)	−0·1001 (4)	0·398 (1)	0·6877 (5)	3·3 (1)
C(2)	−0·0644 (4)	0·593 (1)	0·7765 (5)	3·5 (1)
C(3)	0·0366 (4)	0·614 (1)	0·8251 (5)	3·8 (1)
C(4)	0·1091 (4)	0·448 (1)	0·7895 (6)	4·0 (1)
C(5)	0·0788 (4)	0·265 (1)	0·7044 (5)	3·4 (1)
C(6)	−0·0272 (4)	0·236 (1)	0·6523 (5)	3·4 (1)
Molecule (II)				
Cl	0·3951 (1)	0·1065 (4)	0·5342 (2)	5·23 (4)
O(1)	0·3699 (3)	0·728 (1)	0·8013 (5)	5·3 (1)
O(2)	0·6599 (4)	0·740 (1)	1·0333 (5)	5·8 (1)
O(3)	0·7705 (3)	0·460 (1)	1·0155 (4)	5·6 (1)
N(1)	0·4658 (4)	0·727 (1)	0·8827 (5)	4·4 (1)
N(2)	0·3583 (4)	0·552 (1)	0·7075 (5)	4·7 (1)
N(3)	0·6866 (3)	0·551 (1)	0·9830 (4)	4·1 (1)
C(1)	0·5134 (4)	0·542 (1)	0·8383 (5)	3·2 (1)
C(2)	0·6135 (4)	0·445 (1)	0·8781 (5)	3·2 (1)
C(3)	0·6406 (4)	0·246 (1)	0·8141 (5)	3·8 (1)
C(4)	0·5737 (4)	0·141 (1)	0·7065 (5)	3·9 (1)
C(5)	0·4785 (4)	0·226 (1)	0·6648 (5)	3·7 (1)
C(6)	0·4468 (4)	0·437 (1)	0·7313 (5)	3·4 (1)

Table 2. *Bond lengths* (Å) *and bond angles* (°)

	(I)	(II)		(I)	(II)
Cl–C(5)	1·721 (6)	1·718 (5)	N(3)–C(2)	1·470 (8)	1·444 (7)
O(1)–N(1)	1·384 (8)	1·391 (6)	C(1)–C(2)	1·432 (8)	1·421 (8)
O(1)–N(2)	1·375 (7)	1·368 (8)	C(1)–C(6)	1·423 (8)	1·413 (7)
O(2)–N(3)	1·231 (7)	1·244 (9)	C(2)–C(3)	1·349 (7)	1·365 (9)
O(3)–N(3)	1·218 (7)	1·210 (6)	C(3)–C(4)	1·435 (9)	1·419 (8)
N(1)–C(1)	1·328 (7)	1·328 (8)	C(4)–C(5)	1·349 (9)	1·341 (8)
N(2)–C(6)	1·309 (8)	1·318 (7)	C(5)–C(6)	1·421 (7)	1·455 (9)
N(1)–O(1)–N(2)	112·7 (4)	113·7 (5)	N(3)–C(2)–C(1)	120·4 (4)	121·8 (5)
O(1)–N(1)–C(1)	104·2 (5)	103·3 (4)	N(3)–C(2)–C(3)	120·5 (5)	119·6 (5)
O(1)–N(2)–C(6)	104·5 (5)	103·4 (4)	C(1)–C(2)–C(3)	119·1 (5)	118·6 (5)
O(2)–N(3)–O(3)	125·3 (6)	123·1 (5)	C(2)–C(3)–C(4)	121·7 (6)	122·1 (6)
O(2)–N(3)–C(2)	116·8 (6)	117·0 (5)	C(3)–C(4)–C(5)	121·2 (5)	121·7 (6)
O(3)–N(3)–C(2)	117·9 (5)	119·9 (5)	C(4)–C(5)–C(6)	118·5 (5)	117·6 (5)
N(1)–C(1)–C(2)	132·7 (6)	131·9 (5)	C(1)–C(6)–C(5)	121·1 (5)	120·9 (5)
N(1)–C(1)–C(6)	108·7 (5)	109·0 (4)	C(2)–C(1)–C(6)	118·6 (4)	119·1 (5)
N(2)–C(6)–C(5)	128·9 (6)	128·5 (5)	Cl–C(5)–C(4)	122·8 (5)	123·4 (5)
N(2)–C(6)–C(1)	110·0 (5)	110·6 (5)	Cl–C(5)–C(6)	118·7 (5)	119·0 (4)

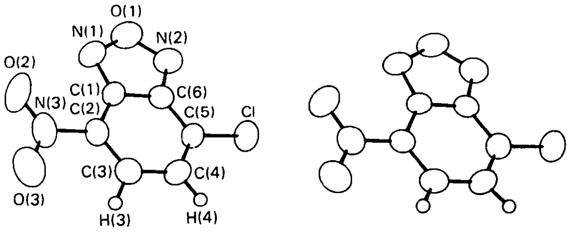

Fig. 1. An *ORTEP* drawing of molecules (I) (left) and (II) (right), and numbering of atoms for the two independent molecules in the asymmetric unit. The atoms are depicted with 50% probability boundary ellipses.

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* Lists of structure factors, anisotropic temperature factors, least-squares planes and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44507 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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).

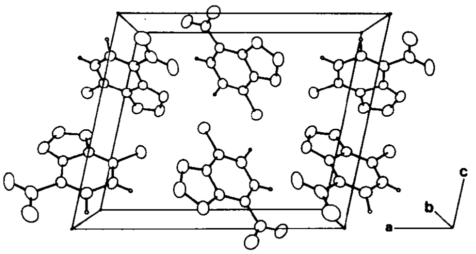

Fig. 2. Packing diagram viewed along the *b* axis.

Examination of the packing diagram (Fig. 2) reveals that only the N(1$^{\rm i}$)···Cl$^{\rm ii}$ [(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 O(2$^{\rm i}$)···C(2$^{\rm ii}$) [(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 Cl$^{\rm i}$···Cl$^{\rm ii}$ [(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.

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

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

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

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

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