Acta Cryst. (1972). B**28**, 2424

The Conformation of Non-Aromatic Ring Compounds. LXXVI.* The Crystal and Molecular Structure of 2-*p*-Nitrophenyl-1,3-Oxathiane

BY N. DE WOLF, G. C. VERSCHOOR AND C. ROMERS

Department of Chemistry, X-ray and Electron Diffraction Section, University of Leiden, Postbox 75, Leiden, The Netherlands

(*Received* 28 *February* 1972)

Crystals of 2-*p*-nitrophenyl-1,3-oxathiane are monoclinic. The space group is $P2_1/n$, the lattice constants are $a=17·248$, $b=11·563$, $c=10·782$ Å and $\beta=100·24°$. The unit cell contains eight molecules. The structure was solved by Patterson methods. Refinement was accomplished by least-squares techniques using photographic and diffractometer data (Cu $K\alpha$ radiation). The final R value is 6·92% for 1889 non-zero terms. Nearly all intramolecular bond distances and valency angles are observed in the range of expected values. The phenyl group is in an equatorial position with respect to the chair-shaped oxathiane ring. An analysis of the thermal motion points to positional disorder of several atoms in the oxathiane ring and the nitrogroup. The observed structure is an average of at least two conformations.

Introduction

This paper is a continuation of earlier reports (de Wolf, Romers & Altona, 1967; De Kok & Romers, 1970) on the crystal structure and the conformation of 1,4- and 1,3-dioxanes, dithianes and oxathianes. As explained elsewhere (Romers, Altona, Buys & Havinga, 1969) detailed investigations of these molecules have been carried out in solutions by applying combined techniques of Raman, infrared and n.m.r. spectra and electric dipole moments.

It has been shown by Buys (1969), on the basis of a method developed earlier (Lambert, 1967), that the ratio of vicinal coupling constants $J(trans)/J(cis)$ of protons for six-membered ring compounds with a $-CH_2-CH_2-$ or a $-CH_2-CHX-$ fragment permits the calculation of the endocyclic torsion angle in that part of the molecule. With this method mean values of 58 and 60° were obtained (de Wolf & Buys, 1970; de Wolf, Wepster & Havinga, 1972) for the endocyclic torsion angles of $O-CH_2-CH_2-CH_2$ and $S-CH_2-CH_2-CH_2$ fragments of 1,3-oxathiane and a number of 2-substituted derivatives.

It thus seems that 1,3-oxathiane is most puckered in the vicinity of the sulphur atom. On the basis of a similar method Gelan, Swaelens & Anteunis (1970) found, however, that 2,4,6-trisubstituted 1,3-oxathianes are most staggered about the carbon–carbon bond near the oxygen atom. They obtained mean endocyclic torsion angles of 59 and 53° for the O- and S-sides respectively. Inspection of Dreiding models by these authors and framework molecular models by de Wolf & Buys indicates the possible existence of two chair forms: one with the largest puckering on the O-side, the other being most puckered on the S-side. On account of these models as well as n.m.r. results the latter authors suggest three possibilities:

(1) the chair conformation of 1,3-oxathiane is rigid with a geometry almost intermediate between the two model forms;

(2) there are two chair forms with different geometry and enthalpy separated by a significant energy barrier giving rise to a conformational equilibrium in solutions;

(3) the two forms are separated by a very low barrier thus yielding a rather flexible chair form.

Since they lack the proper values for valency angles, Dreiding and framework molecular models are rather inadequate for predicting conformations of molecules in this type of compound. Therefore it was thought necessary to verify the quoted suggestions and the predicted torsion angles by an X-ray analysis of a 2-substituted 1,3-oxathiane compound. From a wide range of derivatives 2-*p*-nitrophenyl-1,3-oxathiane (hereafter NPD) was chosen on account of its yielding single crystals suitable for X-ray diffraction work.

Experimental

NPO was prepared by refluxing *p*-nitrobenzaldehyde and 3-hydroxypropanethiol in benzene solution according to a method described by Marshall & Stevenson (1959). The compound crystallizes from carbon tetrachloride in the form of yellow monoclinic needles elongated along the direction [100]. The crystal was mounted along the needle axis. The cell dimensions were determined from measurements of diffraction angles of the reflexions $h00$, $0k0$ and $00l$ using a three-

Table 1. *Crystallographic data of* 2-*p-nitrophenyl*-1,3-*oxathiane*

$C_{10}H_{11}O_3NS$; melting point 105–106°C; monoclinic $P2_1/n$; $a=17·248$ (7), $b=11·563$ (3), $c=10·782$ (4) Å; $\beta=100·24°$ (5)
$d_{\exp}^{20}=1·38$ g.cm^{-3}, $d_x^{20}=1·41$ g.cm^{-3}, $Z=8$
$F(000)=944$ electrons, $V=2116·1$ Å^3, μ(Cu $K\alpha$)$=25·5$ cm^{-1}.

---

* Part LXXV: Knobler, Romers, Braun & Hornstra (1972).

circle diffractometer (Table 1). The angle β was determined by measuring the χ-difference between reflexions $h00$ and $00l$.

Systematic extinctions in $0k0$ for k odd and $h0l$ for $h+l$ odd indicate the space group $P2_1/n$. The observed density at 20°C (Table 1) corresponds with eight molecules per unit cell.

During the analysis two sets of data (I and II) were used:

I. Reflexion intensities measured with an automatic three-circle diffractometer employing the θ–2θ scan and using Ni-filtered Cu $K\alpha$ radiation ($\lambda = 1{\cdot}54178$ Å). According to the classification rules of Arndt & Willis (1966) the goniostat has normal-beam equatorial diffraction geometry, with χ motion restricted between 0 and $-90°$. The procedure for background measurements, filter corrections and assignments of weights has been extensively described (Verschoor & Keulen, 1971; Portheine, Romers & Rutten, 1972). The crystal used had dimensions $0{\cdot}55 \times 0{\cdot}27 \times 0{\cdot}20$ mm and was oriented along the direction [100]* perpendicular to net plane (100). Owing to the design of the diffractometer and the setting of the crystal a number of low angle reflexions were lacking. Moreover, many high angle reflexions were too weak to be observed. The cause of the latter effect is the apparently high thermal motion (see next section).

The total number of collected reflexions was 3020, of which 1246 were not significantly above background. The reduction to structure-factor moduli was performed in the usual way. With the aid of a computer program designed by de Graaf (1972) an accurate correction for absorption was applied.

II. Additional photographic data collected with the same crystal in the setting along [100]. Equi-inclination Weissenberg techniques using Ni-filtered Cu $K\alpha$ radiation resulted in the recording of six reciprocal layers $0kl$ through $5kl$. The reduction of the eye-estimated reflexion intensities to structure factors was accomplished as usual; an approximate absorption correction assuming cylindrical shape of the crystal was applied. The photographic and diffractometer data were put on a common relative scale by the method of Rae (1965). By assignment of weights 10 and 1 to diffractometer and photographic reflexions respectively, a weighted collection of data (set II) was obtained. The total number of reflexions in set II was 3135, including 1246 non-observed.

Patterson analysis

Inspection of sharpened and unsharpened Patterson functions indicates that the p-nitrophenyl groups are located in planes $(20\bar{2})$ with their central axes N–C(1)–C(4)–C(7) (see Fig. 2 for the numbering of atoms) nearly parallel to [010]. Such an arrangement of successive layers of molecules A and B (Fig. 1) suggests why the unit cell contains two symmetry-independent molecules in the asymmetric unit.

A display of hexagonally arranged peaks in the section through the origin parallel to $(10\bar{1})$ fully confirms this orientation. Since the central axes of the molecules A and B are parallel to [010], a section through the Harker line $\frac{1}{2}y\frac{1}{2}$ parallel to $(10\bar{1})$ should contain a superposition of two hexagonal arrays of peaks, resulting in four possible positions of two molecules. Additional information from this Harker line and the Harker section $x\frac{1}{2}z$ permits the location of the two independent sulphur atoms. It must be pointed out that the Harker peaks of the sulphur atoms were not outstanding and that their choice was not obvious. The search for heavy atoms still lacking was continued with the aid of electron density and difference Fourier maps and resulted in a model with $R = 32{\cdot}9\%$.

Refinement

The least-squares refinement of parameters of non-hydrogen atoms, using data set I, proceeded in a regular way. The atomic scattering factors of carbon (C-valence), nitrogen and oxygen were taken from

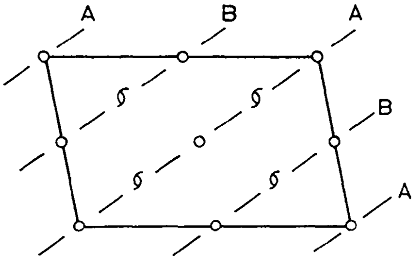

Fig. 1. The idealized arrangement of molecules A and B of NPO in successive layers $(20\bar{2})$.

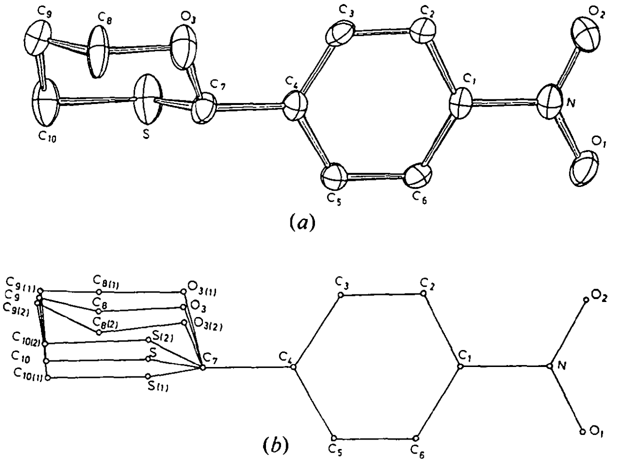

Fig. 2. (a) A perspective view of NPO (molecule B). Thermal ellipsoids are scaled to include a 15% probability (Johnson, 1967). (b) The same view of the positions of the original model and two 'half-atoms' models.

International Tables for X-ray Crystallography (1962). The scattering values of sulphur, corrected for the real part of the anomalous dispersion, were those of Cromer & Waber (1965). For hydrogen the scattering values given by Stewart, Davidson & Simpson (1965) were used. When convergence of heavy-atom positions was reached, subsequent attempts to refine positional and isotropic thermal parameters of the light atoms failed. Large shifts in their positions resulted in C–H distances varying between 0·78 and 1·02 Å, while isotropic thermal parameters were found in the range between 4·8 and 13·5 Å^2. The hydrogen atoms were therefore kept in fixed positions at 0·95 Å from the parent carbon atoms. The isotropic thermal parameters of the light atoms were taken to be equal to those of the corresponding heavy atoms.

The anisotropic refinement of heavy atoms with 3×3 and 6×6 blocks for positional and vibrational parameters and using individual weights as indicated by the diffractometer observations (Portheine, Romers & Rutten, 1972) resulted in an R value of 6·53% (observed reflexions only). Since a part of reciprocal space is not represented in set I, this set is somewhat biased. We therefore repeated the refinement with set II.

The following weighting scheme was then used.

1. Reflexions only measured by the diffractometer were given weights $w=\sigma^{-2}$ as before.
2. Reflexions occurring both in the diffractometer and in the photographic data: average intensities of these reflexions (see experimental part) were also given weights σ^{-2}. The highest and lowest weights were 0·7585 and 0·0006 respectively.
3. Reflexions only observed by photographic methods were assigned weights $w=0·0057$. The application of this procedure ensured that the 'photographic' weights were nearly always smaller (usually by a factor 10) than the 'diffractometer' weights, the nine strongest reflexions excepted. The final R for 1889 non-zero terms was 6·92%.

The positional and vibrational parameters, together with their estimated standard deviations, are listed in Tables 2 and 3. A list of structure factors will be published elsewhere (de Wolf, 1972). It can be seen that a number of thermal parameters, particularly those of atoms in the oxathiane rings and the nitro groups, are suspiciously high. An illustration of this effect can be seen in an *ORTEP* projection (Johnson, 1967) of thermal ellipsoids of molecule *B* (Fig. 2). In view of the proposed possibilities mentioned in the introduction it was deemed necessary to analyse the U_{ij} values in terms of both rigid-body motion and positional disorder.

Applying the procedure of Schomaker & Trueblood (1968), poor agreement between 'observed' and 'calculated' U_{ij} values was obtained. Separate models with and without the nitro groups were considered for the two independent molecules. An examination which uses Hamilton's (1965) R_w ratio test and is described elsewhere (de Graaff, Giesen, Rutten & Romers, 1972)

Table 2. *Positional parameters (fractions of cell edges) and their standard deviations* (Å) *of NPO*

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
C(1*A*)	0·0858	0·005	−0·2355	0·006	0·0960	0·005
C(2*A*)	0·1077	0·006	−0·1759	0·006	−0·0018	0·006
C(3*A*)	0·1162	0·006	−0·0586	0·006	0·0059	0·006
C(4*A*)	0·1037	0·005	0·0005	0·006	0·1125	0·005
C(5*A*)	0·0801	0·006	−0·0603	0·006	0·2085	0·005
C(6*A*)	0·0716	0·006	−0·1789	0·006	0·2003	0·006
C(7*A*)	0·1160	0·006	0·1290	0·006	0·1253	0·006
C(8*A*)	0·1252	0·008	0·3003	0·007	0·0087	0·007
C(9*A*)	0·1983	0·007	0·3480	0·006	0·0904	0·007
C(10*A*)	0·2035	0·006	0·3103	0·007	0·2258	0·007
O(1*A*)	0·0703	0·004	−0·4142	0·004	0·1828	0·004
O(2*A*)	0·0859	0·005	−0·4086	0·004	−0·0097	0·005
O(3*A*)	0·1224	0·005	0·1754	0·004	0·0079	0·004
S(*A*)	0·2048	0·002	0·1566	0·002	0·2411	0·002
N(*A*)	0·0796	0·005	−0·3616	0·005	0·0886	0·005
C(1*B*)	−0·0834	0·005	0·3399	0·005	0·4127	0·005
C(2*B*)	−0·0506	0·005	0·4145	0·005	0·3374	0·005
C(3*B*)	−0·0691	0·005	0·5289	0·005	0·3407	0·005
C(4*B*)	−0·1195	0·005	0·5703	0·005	0·4162	0·005
C(5*B*)	−0·1514	0·005	0·4925	0·005	0·4905	0·005
C(6*B*)	−0·1330	0·005	0·3780	0·005	0·4896	0·005
C(7*B*)	−0·1414	0·005	0·6953	0·005	0·4179	0·006
C(8*B*)	−0·0982	0·006	0·8833	0·005	0·3968	0·009
C(9*B*)	−0·1701	0·007	0·9243	0·006	0·3120	0·007
C(10*B*)	−0·2396	0·006	0·8686	0·006	0·3388	0·008
O(1*B*)	−0·0896	0·004	0·1524	0·003	0·4852	0·004
O(2*B*)	−0·0271	0·005	0·1813	0·004	0·3324	0·004
O(3*B*)	−0·0841	0·004	0·7620	0·004	0·3835	0·005
S(*B*)	−0·2345	0·002	0·7146	0·002	0·3163	0·002
N(*B*)	−0·0649	0·004	0·2154	0·004	0·4096	0·004

Table 3. *Vibrational parameters* U_{ij} (10^{-3} Å^2 *units*) *in the temperature factor* $\exp\left[-2\pi^2 \sum_{ij} h_i h_j a_i^* a_j^* U_{ij}\right]$

Numbers in brackets are e.s.d.'s.

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{31}$
C(1*A*)	60 (4)	85 (4)	63 (4)	1 (6)	12 (6)	26 (6)
C(2*A*)	101 (5)	97 (5)	66 (4)	−12 (7)	−11 (7)	67 (7)
C(3*A*)	108 (5)	77 (4)	66 (4)	2 (7)	23 (7)	74 (7)
C(4*A*)	65 (4)	78 (4)	69 (4)	18 (6)	15 (6)	26 (6)
C(5*A*)	91 (5)	91 (4)	63 (4)	−3 (7)	1 (7)	66 (6)
C(6*A*)	89 (5)	102 (5)	70 (4)	−12 (7)	33 (7)	71 (7)
C(7*A*)	64 (4)	86 (4)	70 (4)	18 (6)	26 (6)	40 (6)
C(8*A*)	142 (7)	98 (5)	86 (5)	21 (9)	33 (8)	14 (9)
C(9*A*)	92 (5)	72 (4)	146 (6)	27 (7)	8 (8)	96 (9)
C(10*A*)	70 (4)	112 (5)	111 (6)	−6 (8)	−29 (9)	21 (8)
O(1*A*)	122 (4)	94 (3)	106 (3)	−27 (5)	36 (5)	88 (6)
O(2*A*)	151 (4)	86 (3)	104 (3)	−15 (6)	−25 (5)	81 (6)
O(3*A*)	142 (4)	66 (3)	77 (3)	11 (5)	25 (4)	32 (5)
S(*A*)	90 (1)	99 (1)	100 (1)	−7 (2)	29 (2)	−8 (2)
N(*A*)	74 (3)	86 (3)	92 (4)	−9 (5)	−5 (6)	33 (6)
C(1*B*)	57 (3)	43 (3)	61 (3)	8 (5)	6 (5)	−2 (5)
C(2*B*)	63 (3)	58 (3)	63 (3)	15 (5)	15 (5)	46 (5)
C(3*B*)	80 (4)	57 (3)	64 (4)	−16 (6)	35 (6)	38 (6)
C(4*B*)	63 (3)	48 (3)	61 (3)	2 (5)	−1 (5)	7 (5)
C(5*B*)	76 (4)	51 (3)	74 (4)	−1 (5)	−1 (6)	59 (6)
C(6*B*)	78 (4)	55 (3)	68 (4)	−16 (6)	19 (6)	58 (6)
C(7*B*)	70 (4)	51 (3)	88 (4)	−11 (5)	22 (6)	34 (6)
C(8*B*)	81 (5)	34 (3)	245 (9)	1 (6)	11 (9)	4 (11)
C(9*B*)	129 (6)	63 (4)	113 (5)	44 (7)	56 (8)	60 (9)
C(10*B*)	71 (4)	71 (4)	170 (7)	29 (7)	1 (9)	−26 (9)
O(1*B*)	126 (4)	50 (2)	101 (3)	−6 (5)	27 (4)	43 (5)
O(2*B*)	144 (4)	73 (3)	102 (3)	67 (5)	−12 (5)	84 (6)
O(3*B*)	71 (3)	53 (2)	211 (5)	4 (4)	35 (6)	63 (6)
S(*B*)	75 (1)	63 (1)	176 (2)	−2 (2)	−20 (2)	−55 (2)
N(*B*)	81 (3)	56 (3)	74 (3)	19 (5)	5 (5)	−4 (5)

showed that these rigid-body models could be rejected on all significance levels. We may conclude that rigid-body thermal motion is not responsible for the observed U_{ij} values.

A positional disorder incorporating both rigid molecules (disorder of their centres of gravity) is highly improbable. Such disorder might occur at temperatures near the melting point and would result in still larger thermal parameters. Since the U_{ij} values of C(7*A*), C(7*B*), N(*A*), N(*B*) and the carbon atoms of the aromatic rings are fairly small, it is obvious that only parts of the molecules, *i.e.* the nitro groups and the O–C–C–C–S moieties suffer from positional disorder.

For every heavy atom in the O–C–C–C–S moieties were substituted two 'half' atoms at positions along the major principal axes of the vibrational ellipsoids [Fig. 2(*b*)]. The separation of their positions was estimated by means of formulae proposed by Kartha & Ahmed (1960) and by Vos & Smits (1961). Since, however, the separations were of the order of 0·4 Å, lack of resolution prevented the refinement of this 'half-atoms' model in terms of adequate bond lengths and valency angles. Although an *R* value of 7·3% was obtained, bond lengths and valency angles showed deviations up to 0·2 Å and 10° respectively.

Discussion of the structure

Disregarding the distances C(9*B*)–C(10*B*) and C(7*B*)–O(3*B*) (1·44 and 1·36 Å), the geometry of the two molecules with chair conformations in an assumed ordered structure (Fig 3) is surprisingly good. The valency angles have their expected values and the endocyclic torsion angles about the bonds C(8)–C(9) and C(9)–C(10) are likewise in the range of values observed by n.m.r. methods. The interatomic bond distances are somewhat too small, but one might argue that corrections of the order of 0·01–0·025 Å (as predicted by the rigid-body model) to a large degree improve the result obtained.

On the other hand we know already that predominant rigid-body motion can explain neither the observed thermal parameters nor the discrepancies observed for C(9*B*)–C(10*B*) and C(7*B*)–O(3*B*). The structure resulting from a straightforward least-squares refinement therefore corresponds to a space-average model of at least two conformations separated by a small energy barrier, or to a time-average of pseudo-librating molecules (Altona, Buys & Havinga, 1966) oscillating between a conformation with larger puckering about C(9)–C(10) and one with larger puckering about C(8)–C(9). Unfortunately, X-ray diffraction experiments cannot distinguish between these two cases. Note, however, that whatever the conformation of the molecule, its largest puckering is about the bond C(7)–O(3) and O(3)–C(8), their mean values being 66 and 65° respectively.

In view of disorder or pseudolibration effects the positional standard deviations listed in Table 2 are grossly underestimated. For this reason we give bond lengths and valency angles to only three figures and torsion angles to only two figures. One might argue that at least the length of bond C(9*B*)–C(10*B*) and probably also the length of bond C(7*B*)–O(3*B*) deviate significantly from their expected values (1·53 and 142 Å, respectively). In view of the observed average structure these deviations are, however, not disturbing.

The mean endocyclic torsion angles of the two oxathiane rings are $\bar{\varphi}(A)=60°$ and $\bar{\varphi}(B)=61°$. Apparently the oxathiane ring is more puckered than cyclohexane, having, in the gas phase, endocyclic torsion angles $\varphi=55{\cdot}9°$ (Geise, Buys & Mijlhoff, 1972). It can be seen from Fig. 4 that the puckering of the

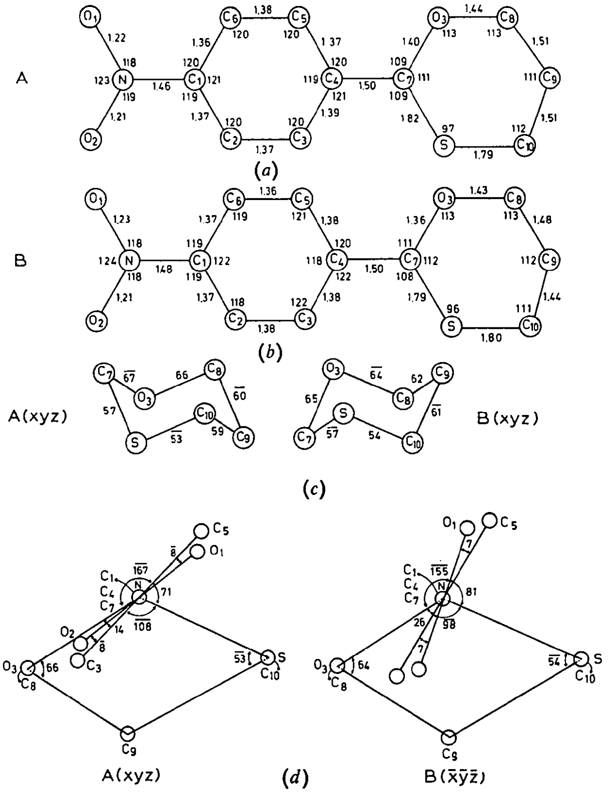

Fig. 3. Bond lengths and valency angles in NPO of (*a*) molecule *A* and (*b*) molecule *B*. (*c*) Endocyclic torsion angles of *A*(*xyz*) and *B*(*xyz*). (*d*) Simultaneous Newman projections along the bonds N–C(1)···C(4)–C(7) and the bonds O(3)–C(8) and S–C(10) of *A*(*xyz*) and *B*(*x̄ȳz̄*).

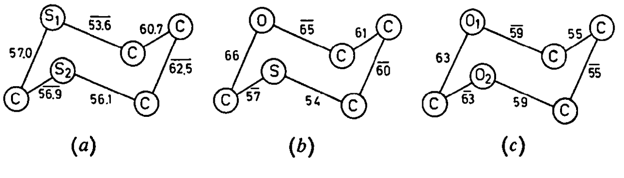

Fig. 4. Torsion angles in the heterocyclic rings of (*a*) 2-phenyl-1,3-dithiane, (*b*) 2-*p*-nitro-phenyl-1,3-oxathiane (mean values) and (*c*) 2-*p*-chlorophenyl-1,3-dioxane.

cyclohexane part of NPO is about the same as that in 2-phenyl-1,3-dithiane (Kalff & Romers, 1966) but larger than that in 2-*p*-chlorophenyl-1,3-dioxane (de Kok & Romers, 1970).

The mean torsion angles about C(8)–C(9) and C(9)–C(10) (averaged over *A* and *B*) are 61 and 60° respectively. These values agree with previously obtained values by n.m.r. methods (59 and 61°; de Wolf, Wepster & Havinga, 1972).

Apart from the orientation of the nitro groups the molecules *A*(*xyz*) and *B*(*xyz*) are approximately mirror images. In order to reveal the geometrical differences between *A* and *B*, simultaneous Newman projections along the nearly collinear bonds N–C(1)···C(4)–C(7) and the bonds O(3)–C(8) and S–C(10) are depicted in Fig. 3(*d*). Comparison is then made between molecule *A*(*xyz*) and the inverted molecule *B*($\bar{x}\bar{y}\bar{z}$). One observes that the aromatic rings are in equatorial position with respect to the oxathiane rings. They enclose dihedral angles of 14 and 71° with the planes C(4)–C(7)–O(3) and C(4)–C(7)–S respectively in molecule *A*. The corresponding values are 26 and 81° in molecule *B*.

In 2-phenyl-1,3-dithiane the phenyl group is perpendicular to the dithiane ring and in 2-*p*-chlorophenyl-1,3-dioxane the phenyl group is approximately parallel to the dioxane ring. In the NPO molecules the phenyl groups occupy positions [Fig. 3(*d*)] about half way between those found in the former compounds.

Another interesting feature of the structure is that the nitro groups are not coplanar with the phenyl groups. They make dihedral angles of −8 and +7° with the phenyl groups in *A*(*xyz*) and *B*($\bar{x}\bar{y}\bar{z}$) [Fig. 3(*d*)]. Non-coplanarity of nitro groups with respect to phenyl rings was also encountered in other compounds. We mention a value of 9·5° for the compound *p*-dinitrobenzene (Abrahams, 1950) and the mean value of 9·7° observed for tri-(*p*-nitrophenyl)phosphate (Mazhar-Ul-Haque & Caughlan, 1969).

The packing of the molecules is shown in a projection of the structure along [001] in Fig. 5. All intermolecular distances smaller than 4·2 Å have been calculated. Including those contacts involving one or two hydrogen atoms (at calculated positions), the molecules I*A* and I*B* are both surrounded by thirteen neighbours, indicating a close packing according to Kitaigorodsky (1961). If only contacts between non-hydro-

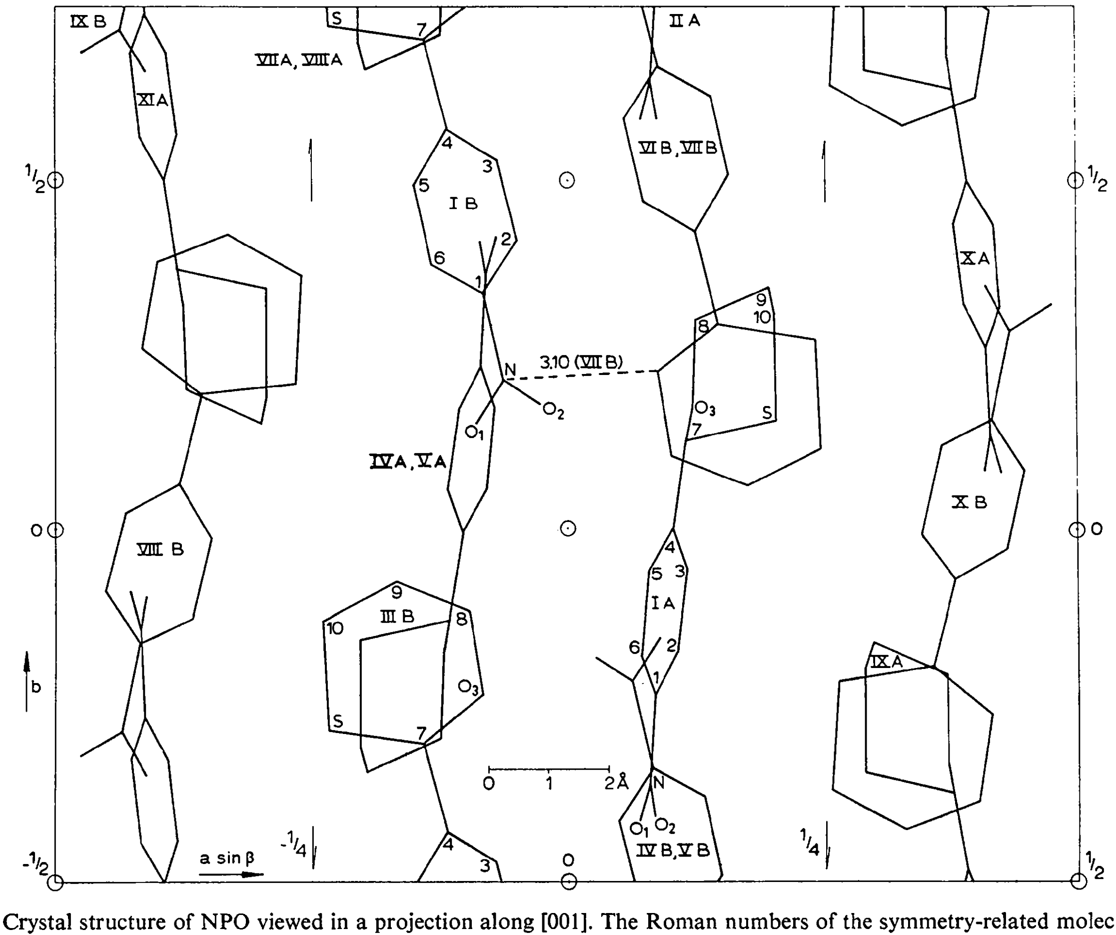

Fig. 5. Crystal structure of NPO viewed in a projection along [001]. The Roman numbers of the symmetry-related molecules are explained in the text. The molecules III*A*, VI*A* and II*B* are not shown in this projection.

gen atoms are considered, molecule I*A* has twelve neighbours within 4·2 Å, while I*B* is surrounded by eleven molecules.

The contacts of I*A* at *xyz* are:

II*A*	x,	$1+y$,	z	III*B*	x,	$-1+y$,	z
III*A*	x,	$-1+y$,	z	IV*B*	$-x$,	$-y$,	$-z$
IV*A*	$-x$,	$-y$,	$-z$	V*B*	$-x$,	$-y$,	$1-z$
VI*A*	$-x$,	$-1-y$,	$-z$	VI*B*	$-x$,	$1-y$,	$-z$
IX*A*	$\frac{1}{2}-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$	VII*B*	$-x$,	$1-y$,	$1-z$
X*A*	$\frac{1}{2}-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$	X*B*	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$-\frac{1}{2}+z$,

while those of molecule I*B* at *xyz* are:

II*B*	x,	$1+y$,	z	II*A*	x,	$1+y$,	z
III*B*	x,	$-1+y$,	z	IV*A*	$-x$,	$-y$,	$-z$
VII*B*	$-x$,	$1-y$,	$1-z$	V*A*	$-x$,	$-y$,	$1-z$
VIII*B*	$-\frac{1}{2}-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$	VII*A*	$-x$,	$1-y$,	$-z$
IX*B*	$-\frac{1}{2}-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$	VIII*A*	$-x$,	$1-y$,	$1-z$
				XI*A*	$-\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$.

It can be seen (Figs. 1 and 5) that the molecules are stacked in planes parallel to $(10\bar{1})$ and (100). The sequence is repeated in the direction [001] after the second but in directions [100] at [101] after the fourth layer. A large number of intermolecular contacts are observed across the layers (100). Nearly all distances in the range between 3·2 and 3·5 Å involve contacts between the atoms O(1), O(2) and N of the nitro group and the atoms C(8), C(9) and O(3) of the oxathiane ring. All these atoms have very large U_{ij} values. Apparently the oxygen atoms belonging to the nitro group share the disorder with the oxathiane ring, the orientation of the nitro group being conditioned by the instantaneous conformation of a neighbouring oxathiane ring. This effect might be considered an argument in favour of a local disorder (space-average model). A similar disorder effect was observed in the structure of β-chloroglutaric anhydride (Koer, de Kok & Romers, 1972) where short intermolecular C–O distances in the range 3·0–3·2 Å are observed between atoms with high thermal parameters.

All calculations were performed on the IBM 360/50 and 360/65 computers of the Central Computing Laboratory of the University of Leiden.

References

Abrahams, S. C. (1950). *Acta Cryst.* **3**, 194.

Altona, C., Buys, H. R. & Havinga, E. (1966). *Rec. Trav. Chim. Pays-Bas*, **85**, 973.

Arndt, U. W. & Willis, B. T. H. (1966). In *Single Crystal Diffractometry*, p. 37. Cambridge Univ. Press.

Buys, H. R. (1969). *Rec. Trav. Chim. Pays-Bas*, **88**, 1003.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104.

Geise, H. J., Buys, H. R. & Mijlhoff, F. C. (1972). *J. Mol. Struct.* In the press.

Gelan, J., Swaelens, G. & Anteunis, M. (1970). *Bull. Soc. Chim. Belges*, **79**, 321.

Graaff, R. A. G. de (1972). Submitted to *Acta Cryst.*

Graaff, R. A. G. de, Giesen, M. T., Rutten, E. W. M. & Romers, C. (1972). *Acta Cryst.* B**28**, 1576,

Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502.

International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.

Johnson, C. K. (1967). *Chem. Div. Annu. Prog. Rept. Oak Ridge Natl. Lab.* 4164, p. 116.

Kalff, H. T. & Romers, C. (1966). *Acta Cryst.* **20**, 490.

Kartha, G. & Ahmed, F. R. (1960). *Acta Cryst.* **13**, 532.

Kitaigorodsky, A. J. (1961). *Organic Chemical Crystallography*. New York: Consultants Bureau.

Knobler, C., Romers, C., Braun, P. B. & Hornstra, J. (1972). *Acta Cryst.* B**28**, 2097.

Koer, F. J., de Kok, A. J. & Romers, C. (1972). *Rec. Trav. Chim. Pays-Bas*. In the press.

Kok, A. J. de & Romers, C. (1970). *Rec. Trav. Chim. Pays-Bas*, **89**, 313.

Lambert, J. B. (1967). *J. Amer. Chem. Soc.* **89**, 1836.

Marshall, J. R. & Stevenson, H. A. (1959). *J. Chem. Soc.* p. 2360.

Mazhar-Ul-Haque & Caughlan, C. N. (1970). *Acta Cryst.* B**26**, 1528.

Portheine, J. C., Romers, C. & Rutten, E. W. M. (1972). *Acta Cryst.* B**28**, 849.

Rae, A. D. (1965). *Acta Cryst.* **19**, 683.

Romers, C., Altona C. Buys, H. R. & Havinga, E. (1969). *Topics in Stereochemistry*, vol. 4, p. 39. Edited by N. L. Allinger, & E. L. Eliel. New York: Interscience.

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

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175.

Verschoor, G. C. & Keulen, E. (1971). *Acta Cryst.* B**27**, 134.

Vos, A. & Smits, D. W. (1961). *Acta Cryst.* **14**, 1299.

Wolf, N. de (1972). Forthcoming thesis. Univ. of Leiden, The Netherlands.

Wolf, N. de & Buys, H. R. (1970). *Tetrahedron Letters* **8**, 551.

Wolf, N. de, Romers, C. & Altona, C. (1967). *Acta Cryst.* **22**, 715.

Wolf, N. de, Wepster, A. H. D. & Havinga, E. (1972). To be published.