

## X-ray Analysis of the Piloty Compounds *trans*- and *cis*-1,4-Dichloro-1,4-dinitrosocyclohexane

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**Abstract.** *trans*-1,4-C<sub>6</sub>H<sub>8</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>,  $M_r = 211.05$ , orthorhombic,  $a = 8.777$  (6),  $b = 10.057$  (7),  $c = 10.133$  (6) Å,  $U = 894$  Å<sup>3</sup>, space group *Pcab*,  $D_m = 1.56$  (by flotation),  $D_x = 1.57$  Mg m<sup>-3</sup>,  $Z = 4$ , Mo *K*α radiation,  $\mu = 0.28$  mm<sup>-1</sup>, 341 independent reflections with intensity greater than  $3\sigma(I)$ ,  $R = 0.033$ ,  $R_w = 0.035$ . The crystal consists of C-nitroso monomers, the molecule is located about a crystallographic centre and the asymmetric unit contains half of the molecule; C–N(O) 1.505 (7), (C)N–O 1.139 (5) Å and C–N–O 116.5 (6)°; the shortest intermolecular O...Cl contact is 3.638 (5) Å; the torsion angle Cl–C–N–O is 2.3°. *cis*-1,4-C<sub>6</sub>H<sub>8</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>,  $M_r = 211.05$ , orthorhombic,  $a = 9.5$ ,  $b = 7.15$ ,  $c = 6.21$  Å,  $U = 422$  Å<sup>3</sup>, space group *Pmmn*,  $D_c = 1.66$  Mg m<sup>-3</sup>,  $Z = 2$ ,  $\mu = 0.30$  mm<sup>-1</sup>, 198 reflections. The crystals consist of internal nitroso dimers with the cyclohexane ring in the boat form; the nitroso dimer has the *mm* symmetry of the space group; N–N 1.31, N–O 1.33 and C–N 1.53 Å, N–N–O 121.5, O–N–C 126 and N–N–C 112.5°. The structure of the *trans* form is based on full three-dimensional counter data. That of the *cis* form was determined some years ago from electron-density projections using Weissenberg film data.

**Introduction.** Piloty & Steinbock (1902) described the preparation of two isomeric 1,4-dichloro-1,4-dinitrosocyclohexane derivatives, blue and colourless, and showed them both to be monomeric. Much later W. Lüttke prepared samples of these for spectroscopic studies from which he deduced that the blue form was all *trans* and centrosymmetric and the colourless form most probably *cis* with the cyclohexane ring in the boat form and an internal dinitroso group. These conclusions were confirmed by X-ray crystallographic studies carried out in 1956 on samples provided by Dr Lüttke and were mentioned in a report by Gowenlock & Lüttke (1958). The X-ray analyses involved measurement of the intensities by eye estimation and calculation of the electron density in each case in all

three projections. These showed the stereochemistry of both molecules very well and proved that in the blue compound the nitroso group is equatorial and chlorine axial, while in the colourless compound, the chlorine is equatorial and the nitroso group axial. In both, the NO–C–Cl unit appeared to be essentially planar.

The blue crystals of the *trans* form from the original preparation have now been re-examined by three-dimensional X-ray measurements. Their investigation is described below. The colourless crystals of the *cis* form have not survived; we include a discussion of some of the early observations pending further study.

**Experimental.** *trans*-1,4-Dichloro-1,4-dinitrosocyclohexane. A blue bipyramidal crystal (0.2 × 0.2 × 0.3 mm), recrystallized from hexane, was sealed in a capillary for X-ray work. After survey photography by oscillation and Weissenberg methods the selected crystal was set up on an Enraf–Nonius CAD-4F diffractometer for data collection. The unit-cell dimensions and orientation matrix were obtained by least squares from the setting angles of 24 reflections, using Mo *K*α radiation from a graphite monochromator. The intensities of reflections with  $\theta \leq 27^\circ$  were collected with  $\omega/2\theta$  scans, a variable scan rate and  $\omega$ -scan angle of  $(1.3 + 0.35 \tan \theta)^\circ$ . 973 independent reflections were measured; 341 of these [ $I > 3\sigma(I)$ ] were corrected for polarization and Lorentz factors and used in the subsequent structure analysis. Inspection of the unsharpened Patterson map revealed the location of the Cl atoms and the subsequent Fourier map gave the positions of all the atoms except H; H atoms were positioned from a difference Fourier map at  $R = 0.058$ . The structure was refined by full-matrix least squares with isotropic temperature factors for the H atoms and anisotropic for the others. In the refinement the bond distances and angles involving H atoms were constrained (Waser, 1963; Rollett, 1969) to be the conventional values with an e.s.d. of 0.1 Å for bond lengths and 2° for bond angles; in addition, the difference in mean-square displacement along the bond direction of the two atoms forming each bond involving H was constrained to be zero with an e.s.d. of 0.01 Å<sup>2</sup>. An overall isotropic extinction parameter

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(Larson, 1967) was included in the final stages of the refinement. Neutral complex atomic scattering factors and corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974). The final conventional  $R$  factor is 0.033 and  $R_w$  0.035. All calculations were performed on the Oxford University ICL 2980 computer with *CRYSTALS* (Carruthers & Watkin, 1980). The final positional and equivalent isotropic thermal parameters are given in Table 1.\* Bond lengths and interbond angles are listed in Table 2 with e.s.d.'s calculated from the full variance-covariance matrix and selected torsion angles are in Table 3.

\* Lists of structure factors and anisotropic thermal parameters for the non-H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38038 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters and isotropic temperature factors ( $\text{\AA}^2$ ) for trans-1,4-dichloro-1,4-dinitrosocyclohexane

	$x$	$y$	$z$	$U_{eq}^*/U_{iso}$
Cl(1)	0.2950 (1)	0.0192 (1)	0.0210 (2)	0.0677
N(1)	0.1261 (6)	0.1953 (5)	0.1651 (5)	0.0666
O(1)	0.2463 (6)	0.2293 (5)	0.1907 (5)	0.0905
C(1)	0.0232 (6)	-0.0249 (5)	0.1414 (5)	0.0500
C(2)	0.1130 (5)	0.0813 (5)	0.0695 (5)	0.0467
C(3)	0.0279 (5)	0.1350 (5)	-0.0490 (5)	0.0474
H(11)	0.086 (3)	-0.062 (3)	0.213 (2)	0.036 (9)
H(12)	-0.068 (2)	0.015 (3)	0.182 (3)	0.05 (1)
H(31)	0.093 (3)	0.198 (3)	-0.099 (3)	0.042 (9)
H(32)	-0.063 (2)	0.184 (3)	-0.018 (3)	0.044 (9)

\* For non-H atoms  $U_{eq} = (U_1 U_2 U_3)^{1/3}$ , where  $U_1$ ,  $U_2$  and  $U_3$  are the mean-square displacements ( $\text{\AA}^2$ ) along each of the principal axes of the thermal ellipsoid. Mean e.s.d. is 0.003  $\text{\AA}^2$ .

Table 2. Bond distances ( $\text{\AA}$ ) and interbond angles ( $^\circ$ ) for trans-1,4-dichloro-1,4-dinitrosocyclohexane, with e.s.d.'s

C(3')-C(1)	1.518 (7)	C(2)-Cl(1)	1.784 (5)
C(1)-C(2)	1.514 (7)	C(2)-N(1)	1.505 (7)
C(2)-C(3)	1.514 (6)	N(1)-O(1)	1.139 (5)
C(3')-C(1)-C(2)	111.8 (4)	C(3)-C(2)-Cl(1)	110.4 (4)
C(1)-C(2)-C(3)	112.1 (5)	C(3)-C(2)-N(1)	106.1 (4)
C(2)-C(3)-C(1')	112.1 (4)	N(1)-C(2)-Cl(1)	112.0 (4)
C(1)-C(2)-Cl(1)	110.6 (4)	C(2)-N(1)-O(1)	116.5 (6)
C(1)-C(2)-N(1)	105.5 (5)		

Symmetry code: (i)  $-x, -y, -z$ .

Table 3. Selected torsion angles ( $^\circ$ )

Cl(1)-C(2)-N(1)-O(1)	2.3 (8)	O(1)-N(1)-C(2)-C(1)	122.6 (8)
O(1)-N(1)-C(2)-C(3)	-118.3 (10)		

**Discussion.** *trans*-1,4-Dichloro-1,4-dinitrosocyclohexane. A perspective drawing of one molecule is shown in Fig. 1. Calculation of the intermolecular distances showed that crystals of the title compound contained isolated C-nitroso monomers. The shortest intermolecular non-bonded contacts for N, O and Cl atoms are N(1)···H(11) ( $x, -\frac{1}{2} + y, -\frac{1}{2} - z$ ) 2.77, O(1)···H(31) ( $-\frac{1}{2} - x, y, -\frac{1}{2} + z$ ) 2.59 and Cl(1)···H(12) ( $-x, -y, -z$ ) 2.88  $\text{\AA}$ . Since all of these distances are greater than the corresponding sum of the van der Waals radii for N···H, O···H and Cl···H systems, the molecule falls into the group of C-nitroso compounds which do not exhibit any intermolecular bonding. Fig. 2 shows the projection drawing of the molecular packing on (010).

Table 4 lists some relevant bond lengths and angles of related aromatic and aliphatic C-nitroso monomers. The N(1)-O(1) bond distance (1.139  $\text{\AA}$ ) in the title compound is significantly shorter than the values of 1.21, 1.213, 1.229 and 1.23  $\text{\AA}$  reported for (V), (VI), (VII) and (VIII); however, when compared with some aliphatic systems, the agreement is good. The N-O bond length reported for (II), 1.16  $\text{\AA}$ , is almost the same as that in the title compound. The lengths from microwave measurements, 1.198 for (III) and 1.211  $\text{\AA}$  for (IV), are about 0.06  $\text{\AA}$  longer than the corresponding value in (I). As expected from the variation of the C-N bond length with that of the N-O length

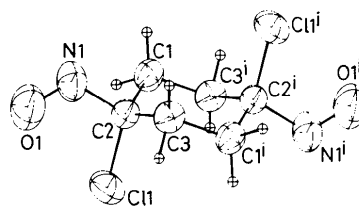


Fig. 1. Perspective view of one molecule of trans-1,4-dichloro-1,4-dinitrosocyclohexane; thermal ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radius. Symmetry code: (i)  $-x, -y, -z$ .

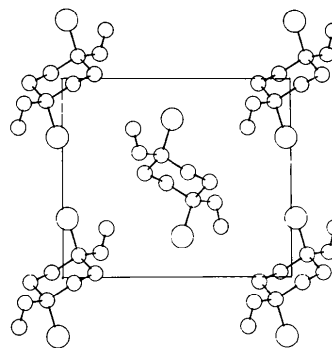
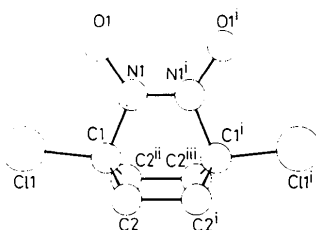
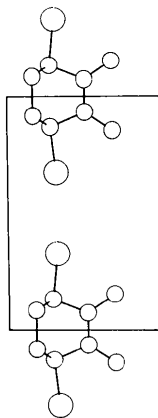


Fig. 2. Projection of part of the molecular packing on (010) for trans-1,4-dichloro-1,4-dinitrosocyclohexane. The  $x$  axis points up the page, the  $z$  axis to the right.

Table 4. Selected dimensions of some nitroso monomers

		N—O (Å)	C—N (Å)	C—N—O (°)
(I)	This work	1.139 (5)	1.505 (7)	116.5 (6)
(II)	10-Bromo-2-chloro-2-nitrosocamphane (Ferguson, Fritchie, Robertson & Sim, 1961)	1.16	1.52	118
(III)	Trifluoronitrosomethane (Turner & Cox, 1976)	1.198	1.510	112.4
(IV)	Nitrosomethane (Turner & Cox, 1978)	1.211	1.482	113.2
(V)	<i>p</i> -Iodonitrosobenzene (Miao & Prout, 1981)	1.21	1.43	113.2
(VI)	5-Nitroso-4-phenylbenzothiothiophene (Prout & Miao, 1982 <i>a</i> )	1.213	1.419	113.8
(VII)	Ethyl <i>trans-m</i> -nitrosocinnamate (Talberg, 1978)	1.229	1.451	113.5
(VIII)	2-Methyl-6-nitroso-7-phenethyl-1,3-benzothiazole (Prout & Miao, 1982 <i>b</i> )	1.23	1.41	114.7

Fig. 3. Perspective view of one molecule of *cis*-1,4-dichloro-1,4-dinitrosocyclohexane. Symmetry code: (i)  $-x, y, z$ ; (ii)  $x, -y, z$ ; (iii)  $-x, -y, z$ .Fig. 4. Projection of part of the molecular packing on (010) for *cis*-1,4-dichloro-1,4-dinitrosocyclohexane. The molecule illustrated in Fig. 3 is now seen projected onto the mirror plane at  $y = 0$ . The  $x$  axis points up the page, the  $z$  axis to the right.

for C-nitroso systems, a long C(2)—N(1) distance of 1.505 Å was found in this work. It is appreciably longer than those found for (V), (VI), (VII) and (VIII), and comparable with the values reported for (II) (1.52 Å), (III) (1.510 Å) and (IV) (1.482 Å). The C—N—O bond angle of 116.5° found in this work is consistent with 118° found in (II), and about 3° larger than the others listed in Table 4. It is, however, not appreciably different from the average of 114° found

for C-nitroso monomers. A characteristic feature of the structure is the coplanarity of the Cl(1)—C(2)—N(1)—O(1) group, as shown by the small torsion angle of 2.3° (see Table 3). The fact that C(1) and C(3) are equidistant (at +1.26 and -1.25 Å) from the plane of the Cl(1)—C(2)—N(1)—O(1) group seems to indicate that Cl(1) is preferentially attracted by O(1), considering the short intramolecular Cl(1)···O(1) contact of 2.754 Å. A similar short Cl···O contact of 2.71 Å was observed in compound (II). The dimensions of the remainder of the molecule are as expected.

*cis*-1,4-Dichloro-1,4-dinitrosocyclohexane. Originally two modifications were found: one in the original preparation and a second in a sample obtained by cooling a solution in boiling methanol. The first crystals appeared usually twinned; approximate lattice constants were  $a = 19.25$ ,  $b = 7.9$ ,  $c = 12.4$  Å,  $Z = \sim 8$ . The second form was orthorhombic,  $a = 9.5$ ,  $b = 7.15$ ,  $c = 6.21$  Å,  $Z = 2$  and was studied further. The space group approximated closely to *Pmnm*; however, three very weak  $hk0$  reflections were observed for which  $h + k \neq 2n$ . This space group required the molecule to have two planes of symmetry, consistent with a regular boat form of the cyclohexane ring and the solution from the electron-density projections conformed with this symmetry; the parameters reached are given below. Standard deviations were not estimated but positional errors of at least 0.1 Å can be expected.

	$x$	$y$	$z$
Cl(1)	0.325	0	0.319
O(1)	0.147	0	0.691
N(1)	0.069	0	0.513
C(1)	0.130	0	0.286
C(2)	0.083	0.181	0.174

It seems possible, however, that the high symmetry is due to disorder in the crystal, involving random packing of molecules of slightly lower symmetry. A perspective drawing of one molecule is shown in Fig. 3 and Fig. 4 gives the projection of the molecular packing on (010). We hope that it will be possible to re-examine both crystalline forms from new preparations.

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### (E)-1-(2-Bromo-4,5-dimethoxyphenyl)-2-(3,4-dimethoxyphenyl)ethylene

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**Abstract.**  $C_{18}H_{19}BrO_4$ ,  $M_r = 379.26$ , monoclinic,  $C2/c$ ,  $a = 28.65$  (3),  $b = 9.340$  (5),  $c = 12.795$  (9) Å,  $\beta = 95.05$  (7)°,  $V = 3410$  (4) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.48$  Mg m<sup>-3</sup>,  $F(000) = 1552$ , Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å),  $\mu(\text{Mo } K\alpha) = 2.58$  mm<sup>-1</sup>. Final  $R = 0.047$  for 1384 observed reflections. The molecule is in the *trans* form and the bromobenzene ring shows a slight distortion.

**Introduction.** In the course of studies directed towards the synthesis of 3-arylisoquinolines by the Bischler–Napieralski reaction (Fodor & Nagubandi, 1980), we have obtained several symmetrical and asymmetrical stilbenes (Lete, 1981). The crystal structure determination of the title compound was undertaken to find out the correct substitution pattern, which could not be unambiguously inferred from chemical or spectroscopic evidence.

Colourless plate-like crystals were grown from methanol. Cell parameters for use in the intensity data collection were calculated by a least-squares analysis of

the angular settings of 15 reflections. Intensities of 2525 independent reflections with  $2\theta < 47^\circ$  were collected from a crystal with dimensions  $0.4 \times 0.2 \times 0.04$  mm on a Syntex  $P2_1$  diffractometer by an  $\omega$  scan with graphite-monochromatized Mo  $K\alpha$  radiation. The intensity of one standard reflection measured every 50 reflections showed no significant variation. 1384 reflections with  $I > 2.5\sigma(I)$  were considered as observed and included in the refinement. Corrections were made for the Lorentz and polarization effects, but not for absorption.

The structure was solved by Patterson and Fourier methods. Full-matrix least-squares refinement with *SHELX* (Sheldrick, 1976) was completed with anisotropic thermal parameters for non-hydrogen atoms. The H atoms were included at the final stage of the refinement in calculated positions with an overall isotropic temperature factor. The weighting scheme was  $w = K/[\sigma^2(F) + 0.0007(F)^2]$ . The final  $R$  was 0.047. Table 1‡ gives the final atomic coordinates with

‡ Lists of structure factors, anisotropic thermal parameters and H atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38029 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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