

Discussion. Table 1 lists the fractional atomic coordinates of the non-H atoms,* Table 2 the bond lengths and angles. Fig. 1 shows selected torsion angles.

The structure of the title compound is illustrated in Fig. 2, which includes the atomic numbering scheme. As indicated by the torsion angles (Fig. 1) and bond distances (Table 2), the eight-membered ring shows approximate *m* symmetry with the pseudoplane including the C3–O1 vector. The five-membered ring has an approximate twofold rotation axis bisecting the O1—C6 bond and the C8 atom. The molecule shows intramolecular hydrogen bonding: O2—H1...O3 2.715 (5) Å (Fig. 2). Fig. 3 gives a representation of the hydrogen-bonding scheme; the donor–acceptor distance is 2.839 (5) Å. The crystal structure is stabilized by extensive hydrogen bonding, with a specific interaction between the hydroxyl

group O3H of one molecule and O2H of another, forming hydrogen-bonded chains along the *b* axis.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52277 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structures of Substituted Olefins. I. (Z)-2-Nitro-1,2-diphenylvinyl Thiocyanate

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Abstract. C₁₅H₁₀N₂O₂S, *M_r* = 282.3, orthorhombic, *Pbca*, *a* = 15.467 (3), *b* = 16.251 (4), *c* = 11.235 (1) Å, *V* = 2824.0 (9) Å³, *Z* = 8, *D_x* = 1.328 g cm⁻³, λ(Mo *Kα*) = 0.71073 Å, μ = 1.87 cm⁻¹, *F*(000) = 1168, *T* = 298 K, *R* = 0.040 for 1394 unique reflections with *I* > 3σ(*I*). The C atoms of the C=C double bond, the N and O atoms of nitro group, and the S atom of the thiocyanate group form a nearly planar backbone. The two phenyl groups are nearly perpendicular to the backbone of the molecule.

Introduction. The configuration of olefinic compounds can be determined by various methods such as ¹H NMR, IR and dipole-moment measurements. These methods are occasionally not sufficient to give all structural information, while X-ray structure analysis can provide the absolute structure. (Z)-2-Nitro-1,2-diphenylvinyl thiocyanate is one of a series of multiply substituted olefins investigated for biological activity. Its configuration has significant

implications in nucleophilic vinylic substitution. Its published *trans*-diphenyl configuration (Rappoport & Topol, 1980) is apparently in error. These two aspects will be presented in detail elsewhere.

Experimental. A pale-yellow single crystal having dimensions 0.25 × 0.33 × 0.35 mm was sealed in a thin-walled glass capillary. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo *Kα* radiation [λ(*Kα*₁) = 0.70930, λ(*Kα*₂) = 0.71359 Å], was used for collecting intensity data. Unit-cell parameters were determined by least-squares refinement of 25 reflections (10 ≤ θ ≤ 16°). Data collection was conducted at room temperature in ω–2θ scan mode using variable rate, θ_{max} = 25° for the range 0 ≤ *h* ≤ 18, 0 ≤ *k* ≤ 19, 0 ≤ *l* ≤ 13, three reflections monitored every hour over the course of data collection for which a linear correction (maximum correction factor 1.004) was applied for 1582 intensities.

Table 1. Positional parameters and equivalent isotropic thermal parameters for (Z)-2-nitro-1,2-diphenylvinyl thiocyanate

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U_{eq}(\text{\AA}^2)$
S	0.0797	0.1858 (1)	0.0755 (1)	0.051
C(1)	0.1791 (2)	0.1405 (2)	0.0339 (3)	0.036 (1)
C(2)	0.1834 (2)	0.0745 (2)	-0.0369 (3)	0.039 (1)
C(3)	0.1169 (2)	0.2562 (2)	0.1752 (3)	0.058 (2)
N(1)	0.1311 (2)	0.3061 (2)	0.2435 (3)	0.090 (3)
N(2)	0.1042 (2)	0.0395 (2)	-0.0837 (2)	0.047 (1)
O(1)	0.0356 (1)	0.0744 (1)	-0.0619 (2)	0.055 (1)
O(2)	0.1084 (2)	-0.0228 (2)	-0.1431 (3)	0.080 (2)
C(11)	0.2594 (2)	0.1819 (2)	0.0753 (3)	0.036 (1)
C(12)	0.2877 (2)	0.2515 (2)	0.0153 (3)	0.048 (2)
C(13)	0.3621 (2)	0.2910 (2)	0.0528 (3)	0.058 (2)
C(14)	0.4075 (2)	0.2616 (2)	0.1501 (3)	0.055 (2)
C(15)	0.3795 (2)	0.1933 (2)	0.2087 (3)	0.058 (2)
C(16)	0.3044 (2)	0.1526 (2)	0.1724 (3)	0.050 (2)
C(21)	0.2656 (2)	0.0349 (2)	-0.0767 (3)	0.043 (1)
C(22)	0.3055 (2)	0.0621 (2)	-0.1779 (3)	0.064 (2)
C(23)	0.3831 (3)	0.0265 (3)	-0.2137 (4)	0.081 (3)
C(24)	0.4197 (3)	-0.0349 (3)	-0.1487 (4)	0.081 (3)
C(25)	0.3795 (3)	-0.0620 (3)	-0.0476 (5)	0.098 (4)
C(26)	0.3019 (3)	-0.0270 (2)	-0.0119 (4)	0.074 (2)

Table 2. Bond distances (\AA) and angles ($^\circ$) for (Z)-2-nitro-1,2-diphenylvinyl thiocyanate

S—C(1)	1.767 (3)	C(14)—C(15)	1.362 (5)
S—C(3)	1.700 (4)	C(11)—C(16)	1.379 (4)
C(1)—C(2)	1.337 (4)	C(15)—C(16)	1.397 (4)
N(1)—C(3)	1.138 (4)	C(2)—C(21)	1.494 (4)
N(2)—C(2)	1.450 (4)	C(21)—C(22)	1.368 (4)
N(2)—O(1)	1.228 (3)	C(22)—C(23)	1.391 (5)
N(2)—O(2)	1.214 (3)	C(23)—C(24)	1.359 (6)
C(1)—C(11)	1.488 (4)	C(24)—C(25)	1.368 (6)
C(11)—C(12)	1.387 (4)	C(21)—C(26)	1.362 (5)
C(12)—C(13)	1.384 (4)	C(25)—C(26)	1.389 (5)
C(13)—C(14)	1.385 (5)		
C(3)—S—C(1)	99.2 (1)	C(13)—C(12)—C(11)	119.5 (3)
N(1)—C(3)—S	171.3 (3)	C(14)—C(13)—C(12)	120.2 (3)
C(2)—C(1)—S	122.3 (2)	C(15)—C(14)—C(13)	120.1 (3)
C(11)—C(1)—S	117.1 (2)	C(16)—C(15)—C(14)	120.6 (3)
C(11)—C(1)—C(2)	120.5 (3)	C(15)—C(16)—C(11)	119.1 (3)
N(2)—C(2)—C(1)	119.3 (3)	C(22)—C(21)—C(2)	119.6 (3)
C(21)—C(2)—C(1)	124.5 (3)	C(26)—C(21)—C(2)	120.6 (3)
C(21)—C(2)—N(2)	116.2 (3)	C(26)—C(21)—C(22)	119.8 (3)
O(1)—N(2)—C(2)	118.4 (3)	C(23)—C(22)—C(21)	119.7 (4)
O(2)—N(2)—C(2)	118.8 (3)	C(24)—C(23)—C(22)	120.6 (4)
O(2)—N(2)—O(1)	122.8 (3)	C(25)—C(24)—C(23)	119.5 (4)
C(12)—C(11)—C(1)	118.7 (3)	C(26)—C(25)—C(24)	120.1 (4)
C(16)—C(11)—C(1)	120.8 (3)	C(25)—C(26)—C(21)	120.3 (4)
C(16)—C(11)—C(12)	120.5 (3)		

The crystal structure was determined by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined on *F* using *SHELX76* (Sheldrick, 1976) on an IBM 3083. All atoms were refined by using anisotropic temperature factors, except H atoms. All H atoms were located in a difference Fourier map and idealized with $C-H = 1.08 \text{ \AA}$. The final full-matrix least-squares refinement with anisotropic thermal parameters for all non-H atoms and iso-

tropic thermal parameters for H atoms yielded $R = 0.040$ and $wR = 0.045$ where w is $1.154/[\sigma^2(F) + 0.0011F^2]$.

The number of reflections used in the least-squares refinement [$I > 3\sigma(I)$] was 1394 and the total number of parameters used was 183. The goodness of fit, $S = 1.295$. The maximum shift/e.s.d. ratio in the final cycle of least squares is 0.04 for all parameters. In the final difference Fourier function, the ten largest peaks ($0.19\text{--}0.14 \text{ e \AA}^{-3}$) were all at chemically implausible positions. Atomic scattering factors for all atoms were from *International Tables for X-ray Crystallography* (1974).

Discussion. Positional and thermal parameters are given in Table 1,* and bond lengths and angles for non-H atoms in Table 2. Fig. 1 is a drawing of the molecule showing the atomic numbering scheme (*ORTEP*; Johnson, 1976).

Eight atoms [S, C(1), C(2), N(2), O(1), C(11) and C(21)] form the plane that is defined by the equation $0.0478x + 0.5897y - 0.8062z = 1.2076$, since none of these atoms is displaced by more than $0.092 (2) \text{ \AA}$.

The thiocyanate group is slightly bent out of the backbone plane by $-10.0 (3)^\circ$ and is approximately linear since the bond angle $S-C(3)-N(1)$ is $171.3 (3)^\circ$, which is similar to that in *cis*-3-nitro-2-thiocyanato-2-butene (Carpenter & Park, 1987). The

* Lists of anisotropic thermal parameters, H-atom parameters, least-squares planes, torsion angles and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52494 (13 pp.). Copies may be obtained through The Technical Editor, *International Union of Crystallography*, 5 Abbey Square, Chester CH1 2HU, England.

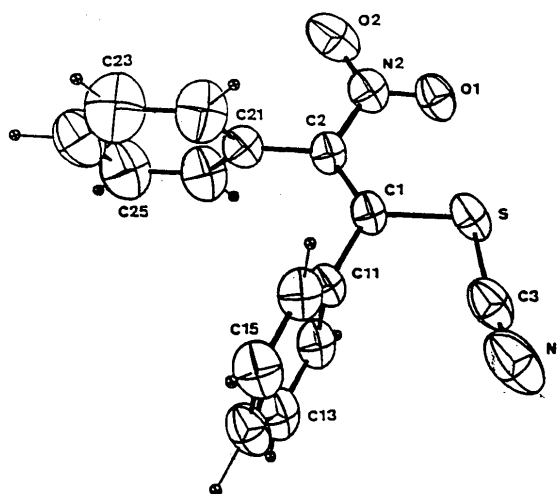


Fig. 1. *ORTEP* (Johnson, 1976) drawing of (Z)-2-nitro-1,2-diphenylvinyl thiocyanate with the atomic numbering scheme and thermal ellipsoids.

plane formed with the nitro group and the molecular backbone is probably the result of a favorable configuration for π -electron delocalization. There also appears to be a strong dipole interaction between S and O(1) as indicated by the short contact distance, 2.476 (3) Å [2.532 (2) Å (Iwasaki, 1986) and 2.501 (2) Å (Iwasaki & Masuko, 1986)].

The configuration of the two phenyl rings is noteworthy. The two phenyl groups are nearly perpendicular to the backbone of the molecule [dihedral angles C(22)—C(21)—C(2)—C(1) -88.3 (4), C(26)—C(21)—C(2)—C(1) 90.5 (4), C(12)—C(11)—C(1)—C(2) 98.0 (4) and C(16)—C(11)—C(1)—C(2) -89.9 (4) $^\circ$] to reduce steric hindrance, which implies that there is very little π - π interaction between the phenyl groups and the molecular backbone.

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Structures of Substituted Olefins. II.* 4-(2-Nitro-1,2-diphenylvinyl)morpholine

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Abstract. $C_{18}H_{18}N_2O_3$, $M_r = 310.35$, monoclinic, $P2_1/n$, $a = 10.476$ (2), $b = 10.680$ (1), $c = 14.357$ (2) Å, $\beta = 95.90$ (1) $^\circ$, $V = 1597.8$ (5) Å³, $Z = 4$, $D_x = 1.29$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.52$ cm⁻¹, $F(000) = 656$, $T = 298$ K, $R = 0.040$ for 1296 unique reflections with $I > 3\sigma(I)$. The central C=C bond is weakened [1.378 (4) Å] and twisted by 23.3 (3) $^\circ$ from the planarity of sp^2 bonding. The bond between the sp^2 carbon and the nitrogen of the morpholine moiety is nearly a double bond [1.353 (4) Å]. The nitro group is twisted by about 24 $^\circ$ from the molecular backbone. The two phenyl groups are rotated by about 60 $^\circ$ from the backbone of the molecule.

Introduction. In search of new lead compounds of biological activity, a series of sterically hindered olefins has been synthesized. Some of them have already been communicated by Carpenter & Park (1987) and Park & Jeong (1990). The X-ray structure of 4-(2-nitro-1,2-diphenylvinyl)morpholine was determined in order to confirm the stereochemistry and to examine the effects of steric hindrance.

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Experimental. A pale-yellow single crystal, 0.20 × 0.30 × 0.43 mm, was mounted in a 0.5 mm diameter thin-walled glass capillary and sealed. Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation [$\lambda(K\alpha_1) = 0.70930$, $\lambda(K\alpha_2) = 0.71359$ Å] was used for the measurement of diffraction intensities. The unit-cell constants were determined by least-squares refinement of 25 reflections with a 2θ range between 13 and 21 $^\circ$. Intensity data were collected within the 2θ range 2–50 $^\circ$ and variable scan rates in $\omega/2\theta$ scan mode for the range $0 \leq h \leq 12$, $0 \leq k \leq 12$, $-16 \leq l \leq 16$ making three intensity checks every hour at room temperature. Maximum $\sin\theta/\lambda$ reached in intensity measurement was 0.63 Å⁻¹; 3151 measured intensities, 1296 unique observed with $I > 3\sigma(I)$.

The crystal structure was solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined using *SHELX76* (Sheldrick, 1976) on an IBM 3083 computer. All H atoms were located in a difference Fourier map and idealized with C—H = 1.08 Å for refinement.

The final full-matrix least-squares refinement with anisotropic thermal parameters for all non-H atoms

* Part I: Park & Jeong (1990).