

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.

* Part I: Park & Jeong (1990).

References

- CARPENTER, G. B. & PARK, K. P. (1987). *Acta Cryst.* **C43**, 1821–1822.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71, 91, 149. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 IWASAKI, F. (1986). *Acta Cryst.* **C42**, 121–124.
 IWASAKI, F. & MASUKO, Y. (1986). *Acta Cryst.* **C42**, 124–127.
 JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
 RAPPOPORT, Z. & TOPOL, A. (1980). *J. Am. Chem. Soc.* **102**, 407–408.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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

Table 1. Positional parameters and equivalent isotropic thermal parameters for 4-(2-nitro-1,2-diphenylvinyl)morpholine

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

	x	y	z	U_{eq}
O(1)	1.0075 (2)	0.2831 (2)	1.0491 (2)	0.0506 (2)
O(2)	1.1437 (2)	0.1310 (2)	1.0624 (2)	0.0609 (2)
N(1)	1.0410 (3)	0.1785 (3)	1.0799 (2)	0.0466 (2)
C(1)	0.9651 (3)	0.1127 (3)	1.1408 (2)	0.0422 (2)
C(2)	0.8351 (3)	0.1345 (3)	1.1383 (2)	0.0399 (2)
N(2)	0.7596 (2)	0.1782 (3)	1.0632 (2)	0.0446 (2)
C(3)	0.6457 (3)	0.2555 (3)	1.0709 (2)	0.0545 (3)
C(4)	0.5344 (3)	0.2044 (5)	1.0066 (3)	0.0684 (3)
O(3)	0.5642 (2)	0.1946 (3)	0.9129 (2)	0.0712 (2)
C(5)	0.6737 (3)	0.1174 (4)	0.9079 (3)	0.0595 (3)
C(6)	0.7903 (3)	0.1669 (3)	0.9665 (2)	0.0502 (3)
C(11)	1.0348 (3)	0.0204 (3)	1.2040 (2)	0.0439 (2)
C(12)	1.0030 (3)	-0.1053 (3)	1.1977 (3)	0.0531 (2)
C(13)	1.0689 (4)	-0.1915 (4)	1.2560 (3)	0.0712 (3)
C(14)	1.1659 (5)	-0.1533 (5)	1.3219 (3)	0.0824 (4)
C(15)	1.1991 (4)	-0.0295 (5)	1.3289 (3)	0.0795 (4)
C(16)	1.1332 (4)	0.0585 (4)	1.2701 (3)	0.0632 (3)
C(21)	0.7669 (3)	0.0986 (3)	1.2209 (2)	0.0403 (2)
C(22)	0.6680 (3)	0.0108 (3)	1.2101 (2)	0.0477 (2)
C(23)	0.6029 (3)	-0.0221 (4)	1.2857 (2)	0.0569 (3)
C(24)	0.6327 (4)	0.0357 (4)	1.3713 (3)	0.0620 (3)
C(25)	0.7297 (4)	0.1225 (4)	1.3824 (2)	0.0586 (3)
C(26)	0.7993 (3)	1.1532 (3)	1.3079 (2)	0.0489 (2)

Table 2. Bond distances (Å), bond angles (°) and selected torsion angles (°) for 4-(2-nitro-1,2-diphenylvinyl)morpholine

N(1)—O(1)	1.240 (3)	C(12)—C(13)	1.381 (5)
N(1)—O(2)	1.239 (3)	C(13)—C(14)	1.377 (6)
N(1)—C(1)	1.426 (4)	C(14)—C(15)	1.369 (6)
C(1)—C(2)	1.378 (4)	C(11)—C(16)	1.389 (5)
N(2)—C(2)	1.353 (4)	C(15)—C(16)	1.398 (6)
N(2)—C(3)	1.465 (4)	C(2)—C(21)	1.496 (4)
N(2)—C(6)	1.461 (4)	C(21)—C(22)	1.395 (4)
C(3)—C(4)	1.513 (5)	C(22)—C(23)	1.385 (4)
O(3)—C(4)	1.416 (4)	C(23)—C(24)	1.381 (5)
O(3)—C(5)	1.421 (4)	C(24)—C(25)	1.373 (5)
C(5)—C(6)	1.506 (5)	C(21)—C(26)	1.389 (4)
C(1)—C(11)	1.480 (4)	C(25)—C(26)	1.394 (5)
C(11)—C(12)	1.384 (5)		
O(2)—N(1)—O(1)	121.2 (3)	C(12)—C(11)—C(1)	120.4 (3)
C(1)—N(1)—O(1)	120.5 (3)	C(16)—C(11)—C(1)	120.6 (3)
C(1)—N(1)—O(2)	118.3 (3)	C(16)—C(11)—C(12)	119.0 (3)
C(2)—C(1)—N(1)	120.8 (3)	C(13)—C(12)—C(11)	120.4 (4)
C(11)—C(1)—N(1)	115.7 (3)	C(14)—C(13)—C(12)	120.4 (4)
C(11)—C(1)—C(2)	123.5 (3)	C(15)—C(14)—C(13)	120.1 (4)
N(2)—C(2)—C(1)	125.1 (3)	C(16)—C(15)—C(14)	119.9 (4)
C(21)—C(2)—C(1)	119.2 (3)	C(15)—C(16)—C(11)	120.2 (4)
C(21)—C(2)—N(2)	115.6 (3)	C(22)—C(21)—C(2)	119.7 (3)
C(3)—N(2)—C(2)	123.2 (3)	C(26)—C(21)—C(2)	120.9 (3)
C(6)—N(2)—C(2)	124.1 (3)	C(26)—C(21)—C(22)	119.4 (3)
C(6)—N(2)—C(3)	112.3 (3)	C(23)—C(22)—C(21)	120.3 (3)
C(4)—C(3)—N(2)	109.4 (3)	C(24)—C(23)—C(22)	119.9 (3)
C(3)—C(4)—O(3)	112.1 (3)	C(25)—C(24)—C(23)	120.1 (3)
C(5)—O(3)—C(4)	110.4 (3)	C(26)—C(25)—C(24)	120.6 (3)
C(6)—C(5)—O(3)	112.4 (3)	C(25)—C(26)—C(21)	119.6 (3)
C(5)—C(6)—N(2)	108.3 (3)		
N(1)—C(1)—C(2)—N(2)	25.30 (49)	C(26)—C(21)—C(2)—C(1)	62.00 (42)
C(11)—C(1)—C(2)—C(21)	21.01 (45)	C(22)—C(21)—C(2)—C(1)	-119.13 (34)
C(12)—C(11)—C(1)—C(2)	61.12 (43)	C(2)—C(1)—N(1)—O(1)	26.03 (45)
C(16)—C(11)—C(1)—C(2)	-119.14 (38)	C(2)—C(1)—N(1)—O(2)	-157.34 (30)

and isotropic thermal parameters for H atoms (226 refined parameters) gave $R = 0.040$ and $wR = 0.042$, where w is $1.65/[\sigma^2(F) + 0.0006F^2]$ and $S = 1.692$, $(\Delta/\sigma)_{\max} < 0.03$ and $(\Delta\rho)_{\max}$ in the final difference Fourier map was $0.13 \text{ e } \text{Å}^{-3}$. Atomic scattering factors for all atoms were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1* and bond distances and angles for non-H atoms are listed in Table 2. Fig. 1 shows the molecular geometry and atom-labelling scheme for the molecule (ORTEP; Johnson, 1976).

The double bond itself and its other substituents are distorted due to steric hindrance. The C(1)—C(2) distance of 1.378 (4) Å is longer than 1.337 (6) Å found in a single —C=C— bond (Dean, 1987), the C(2)—N(2) length of 1.353 (4) Å is somewhat longer than 1.32 Å in —C=N— bonds, and much shorter than 1.475 (10) Å in —C—N= bonds, and the C(1)—N(1) distance, 1.426 (4) Å, is nearly the length of a single C—N bond. C(2), N(2), C(3) and C(6) are coplanar within 0.038 (3) Å. The backbone of the molecule is rotated by about 23°, a result of a

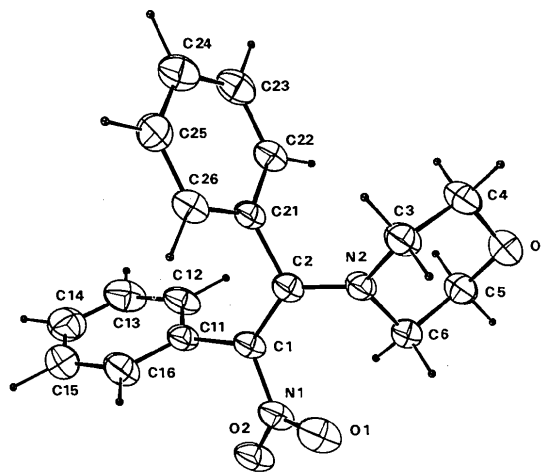


Fig. 1. ORTEP thermal ellipsoid drawing of 4-(2-nitro-1,2-diphenylvinyl)morpholine showing the atom-labelling scheme.

weakened C=C double bond [which is caused by a shortened C(2)—N(2) bond length] and also of steric hindrance around the molecular backbone: the dihedral angles N(1)—C(1)—C(2)—N(2) and C(11)—C(1)—C(2)—C(21) are 25.3 (5) and 21.0 (5)°, respectively. The six atoms C(1), C(2), C(11), C(21),

* 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 52909 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

N(1) and N(2) are not coplanar, and although C(1) and C(2) are located approximately on the mean plane of the six atoms, the displacements of N(1), C(21), N(2) and C(11) are 0.234 (3), 0.235 (3), -0.255 (3) and -0.244 (3) Å, respectively. The two phenyl groups are tilted by about 60° from the mean plane of the molecular backbone.

The plane of the nitro group O(1)—N(1)—O(2) is tilted by about 24° from the plane of N(1)—C(1)—C(11) with O(1) lying 0.453 (3) Å above and O(2) 0.405 (3) Å below this plane (see Fig. 1).

The conformation of the morpholine ring is a regular chair form: C(3), C(4), C(5) and C(6) are coplanar within 0.007 (3) Å and N(2) and O(3) deviate by -0.632 (3) and 0.638 (3) Å from this plane. In conclusion, the striking aspects of the molecule are that the C=C bond is twisted by 23.3°, the nitro group is twisted by about 24° and the two phenyl groups are tilted by 60°, resulting in loss of

significant delocalization energy to relieve the steric hindrance.

References

- CARPENTER, G. B. & PARK, K. P. (1987). *Acta Cryst.* **C43**, 1821–1822.
 DEAN, J. A. (1987). *Handbook of Organic Chemistry*, pp. 3–12. New York: McGraw-Hill.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71, 91, 149. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
 PARK, K. P. & JEONG, J. H. (1990). *Acta Cryst.* **C46**, 1657–1659.
 SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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Ethyl 7-Hydroxy-4-coumarinacetate

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Abstract. C₁₃H₁₂O₅, *M_r* = 248.23, monoclinic, *P*2₁, *a* = 4.698 (5), *b* = 10.277 (3), *c* = 12.009 (2) Å, β = 99.58 (1)°, *V* = 571.7 (6) Å³, *Z* = 2, *D_x* = 1.442 g cm⁻³, λ(Cu Kα) = 1.5418 Å, μ = 8.98 cm⁻¹, *F*(000) = 260, *T* = 298 K, final *R* = 0.037 for 1098 observed reflections. The coumarin moiety is planar and the plane of the ethyl acetate group makes an angle of 88.1 (1)° to it. The crystal structure is stabilized by O—H...O hydrogen bonds: O(7)...O(2ⁱ) = 2.765 (3) Å, O(7)—H...O(2ⁱ) = 156° [(i) 1 - *x*, *y* - 0.5, 2 - *z*].

Introduction. Coumarin derivatives have been found to be useful in solid-state photochemical reactions (Gnanaguru, Ramasubbu, Venkatesan & Ramamurthy, 1985), dye laser studies (Masilamani, 1979) and in a variety of biological studies (Crombie, Jones & Palmer, 1985; Bravic & Bideau, 1978; Valente, Trager & Jensen, 1975). The present study is part of our investigations on coumarin derivatives

involved in photochemical reactions and dye laser activity.

Experimental. Needle-shaped transparent crystals from a mixture of ethanol and chloroform; crystal size 0.5 × 0.3 × 0.3 mm; Enraf-Nonius CAD-4 diffractometer; graphite-monochromated Cu Kα radiation; cell parameters from least-squares treatment of setting angles of 25 reflections with 25 < θ < 35°, ω/2θ scan technique; intensity variation of two standard reflections monitored every 98 reflections less than 3%; total number of reflections measured 1551 with 2θ ≤ 140°, 1098 observed reflections with *I* > 3σ(*I*); range of *hkl*: *h* 0 → 5, *k* 0 → 12 and *l* - 14 → 14; *L_p* correction but absorption ignored; structure solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); refinement on *F* by full-matrix least-squares method; H atoms from difference Fourier map; anisotropic thermal parameters for