SHORT-FORMAT PAPERS

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Structure of (*E*)-3-Bromo-4-nitro-4-phenyl-3-buten-2-one

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Abstract. $C_{10}H_8BrNO_3$, $M_r = 270.08$, orthorhombic, $Pna2_1$, $a = 11.137\ (1)$, $b = 17.361\ (2)$, $c = 5.5641\ (4)$ Å, $V = 1075.8\ (2)$ Å^3, $Z = 4$, $D_x = 1.666$ g cm^{-3}, $F(000) = 536$, $\lambda(\text{Mo}\ K\alpha) = 0.71073$ Å, $\mu = 37.67$ cm^{-1}, $T = 298$ K, $R = 0.034$ for 690 unique reflections with $I \geq 3\sigma(I)$. The nitro group is coplanar with the C═C bond but the additional π bonding of the C═O group and the phenyl ring means that they are twisted relative to the C═C bond plane by about 90 and 79°, respectively.

Experimental. Crystals of the title compound suitable for X-ray diffraction were obtained from $CHCl_3$ solution (Park & Ha, 1991). A pale yellow single crystal, 0.35 × 0.40 × 0.48 mm, was mounted in a 0.5 mm diameter thin-walled glass capillary and sealed. An Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation was used for the measurement of diffraction intensities. The unit-cell parameters were calculated with 25 reflections in the 2θ range 14–25°. Intensity data were recorded in $\omega/2\theta$ scan mode using variable scan rates; $\theta_{\max} = 25°$ for the range $0 \leq h \leq 13$, $0 \leq k \leq 20$, $0 \leq l \leq 6$. Three standard reflections measured after every hour did not reveal any systematic variations higher than 0.09% in intensity at room temperature. The data set collected consisted of 690 reflections above $3\sigma(I)$ out of a total of 1155 reflections. Systematic absence in the data indicated the possible space group $Pna2_1$ ($0kl$; $k + l = 2n + 1$, $h0l$; $h = 2n + 1$).

The structure was solved by the conventional heavy-atom method and difference Fourier technique and refined using *SHELX*76 (Sheldrick, 1976). The final full-matrix least-squares refinement was based on F with anisotropic thermal parameters for all non-H atoms and isotropic thermal parameters for H atoms idealized with a C—H distance of 0.95 Å. 143 refined parameters gave the error indices $R = 0.034$ and $wR = 0.035$ for 690 reflections, where $w = 0.085/[\sigma^2(F) + 0.001318\ (F)^2]$, $S = 0.2827$, $(\Delta/\sigma)_{\max} < 0.04$ and $\Delta\rho_{\max}$ in the final difference Fourier map was 0.42 e Å^{-3}. Atomic scattering factors for all atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic coordinates and equivalent isotropic thermal parameters for non-H atoms are given in Table 1† and selected bond lengths, angles, and some informative torsional angles are listed in Table 2. Fig. 1 shows the molecular geometry and atom-labelling scheme for the molecule drawn using *ORTEP* (Johnson, 1976).

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† Lists of structure factors, anisotropic thermal parameters, H-atom parameters, least-squares-planes data, selected torsion angles and intramolecular distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71155 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1011]

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Table 1. *Positional parameters and equivalent isotropic thermal parameters for* (*E*)-3-*bromo*-4-*nitro*-4-*phenyl*-3-*buten*-2-*one*

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

	x	y	z	U_{eq}
Br	0.2264 (1)	0.2233 (1)	0.2500	0.062 (1)
N	−0.0361 (5)	0.2651 (3)	0.7627 (26)	0.052 (7)
O(1)	0.1142 (8)	0.0934 (3)	0.6503 (15)	0.094 (7)
O(2)	−0.0811 (7)	0.2029 (4)	0.7801 (22)	0.095 (7)
O(3)	−0.0689 (8)	0.3176 (4)	0.8791 (19)	0.114 (8)
C(1)	−0.0239 (10)	0.1035 (6)	0.3245 (20)	0.066 (8)
C(2)	0.0624 (8)	0.1306 (5)	0.5033 (18)	0.050 (6)
C(3)	0.1027 (8)	0.2153 (4)	0.4750 (15)	0.042 (5)
C(4)	0.0616 (7)	0.2773 (4)	0.5893 (15)	0.036 (4)
C(41)	0.1050 (7)	0.3579 (4)	0.5680 (16)	0.038 (5)
C(42)	0.1781 (7)	0.3887 (4)	0.7417 (26)	0.049 (7)
C(43)	0.2178 (9)	0.4642 (5)	0.7261 (34)	0.063 (8)
C(44)	0.1883 (9)	0.5068 (5)	0.5309 (20)	0.062 (7)
C(45)	0.1152 (8)	0.4778 (4)	0.3571 (19)	0.060 (7)
C(46)	0.0716 (8)	0.4023 (5)	0.3739 (18)	0.052 (6)

Table 2. *Selected bond distances* (Å), *bond angles* (°) *and torsion angles* (°) *for* (*E*)-3-*bromo*-4-*nitro*-4-*phenyl*-3-*buten*-2-*one*

Br—C(3)	1.867 (8)	C(1)—C(2)	1.462 (13)
O(1)—C(2)	1.191 (11)	C(2)—C(3)	1.545 (11)
N—O(2)	1.195 (8)	C(3)—C(4)	1.331 (10)
N—O(3)	1.176 (11)	C(4)—C(41)	1.485 (10)
N—C(4)	1.470 (12)		
O(3)—N—O(2)	121.7 (8)	C(4)—C(3)—Br	120.9 (6)
C(4)—N—O(2)	119.6 (9)	C(4)—C(3)—C(2)	128.4 (8)
C(4)—N—O(3)	118.7 (6)	C(3)—C(4)—N	116.8 (6)
C(1)—C(2)—O(1)	127.7 (8)	C(41)—C(4)—N	115.4 (6)
C(3)—C(2)—O(1)	116.4 (9)	C(41)—C(4)—C(3)	127.8 (7)
C(3)—C(2)—C(1)	115.3 (8)	C(42)—C(41)—C(4)	120.3 (8)
C(2)—C(3)—Br	110.7 (6)	C(46)—C(41)—C(4)	120.1 (8)
C(3)—C(4)—C(41)—C(42)	−102 (1)	C(3)—C(4)—C(41)—C(46)	79 (1)
Br—C(3)—C(2)—O(1)	89.1 (9)	C(4)—C(3)—C(2)—O(1)	−90 (1)
Br—C(3)—C(2)—C(1)	−83.3 (9)		

Related literature. For stereochemical studies of nucleophilic vinylic substitution reactions (Park & Ha, 1990, 1991) a series of multiply-substituted nitro olefins were prepared. Their molecular structures were confirmed by X-ray diffraction (Carpenter & Park, 1987; Park & Jeong, 1990*a*, 1990*b*).

Eight atoms [Br, C(2), C(3), C(4), N, O(2), O(3), C(41)] are found to be coplanar and with no atom displaced by more than 0.09 (1) Å from its best plane, which is similar to the situation in (*Z*)-2-nitro-1,2-diphenylvinyl thiocyanate but different from that in 4-(2-nitro-1,2-diphenylvinyl)morpholine (Park & Jeong, 1990*a*, 1990*b*). The phenyl ring is tilted by about 79° from the plane of the molecular backbone. The torsion angles C(3)—C(4)—C(41)—C(46) and C(3)—C(4)—C(41)—C(42) are 79 (1) and −102 (1)°, respectively. This arrangement is caused by steric hindrance between Br and the phenyl ring, and between the phenyl ring and the nitro group resulting in the loss of significant delocalization energy for the molecule. This is also seen in two related compounds. The intramolecular contact distances Br···C(46) 3.620 (9) and O(3)···C(42) 3.11 (1) Å are shorter than the sums of the van der Waals radii (Huheey, 1983).

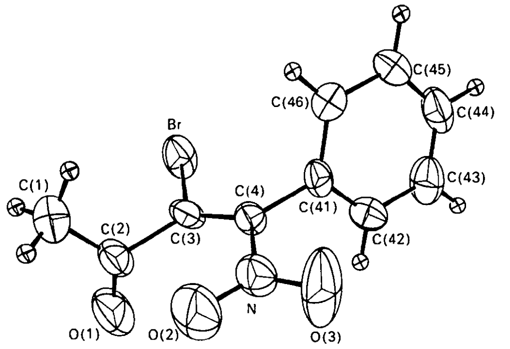

Fig. 1. *ORTEP* drawing of (*E*)-3-bromo-4-nitro-4-phenyl-3-buten-2-one showing the atom-labeling scheme and thermal ellipsoids.

Three atoms of the nitro group are located almost in the plane of the molecular backbone. The plane comprised of the C(1), C(2) and O(1) atoms is nearly perpendicular to the molecular backbone. The dihedral angles Br—C(3)—C(2)—O(1) and Br—C(3)—C(2)—C(1) are 89.1 (9) and −83.3 (9)°, respectively. This results from the steric hindrances between Br and O(1), Br and the methyl group, and O(2) and the methyl group. The distances Br···O(1), Br···C(1) and O(2)···C(1) are 3.407 (7), 3.50 (1) and 3.13 (1) Å, respectively, which are shorter than the sums of the van der Waals radii (Huheey, 1983). In conclusion, the nitro group is coplanar with the C=C bond; the additional π-bonding moieties, C=O and the phenyl ring, are not coplanar with the bond, resulting in loss of delocalization energy in order to relieve the steric hindrance.

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