Fig. 4. Packing of the molecules viewed down the a axis.

respect to the plane of the aryl ring could perhaps be used to examine the magnetic anisotropy effects of the aryl ring on these protons.

The molecular packing viewed down the a axis is shown in Fig. 4. There are no short contacts within 3·5 Å.

many natural products containing this skeleton (*e.g.* Coggon & Sim, 1969). The angular deformations of the phenyl ring caused by the substituents are in keeping with the pattern expected for substituted benzenes (Domenicano, Vaciago & Coulson, 1975). The intramolecular overcrowding of the *ortho* substituents of the phenyl ring is minimized by out-of-plane displacement of the substituents.

The angle between the least-squares planes passing through the phenyl-ring atoms and that of the plane through the atoms C(9), C(10), C(2) and C(5) is 106·6 (5)°. In 1-arylcyclohexane derivatives, the conformation of minimum steric interaction between the aryl and cyclohexane ring atoms is the one where the rings are orthogonal to each other (Allinger, Allinger, Darooge & Greenberg, 1962). Thus, the conformation of the aryl group in structure (3) appears to correspond to the most stable one and the disposition of the bridgehead and the keto–methylene protons with

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Ethyl (Z)-2-Nitro-3-(4-nitrophenyl)acrylate

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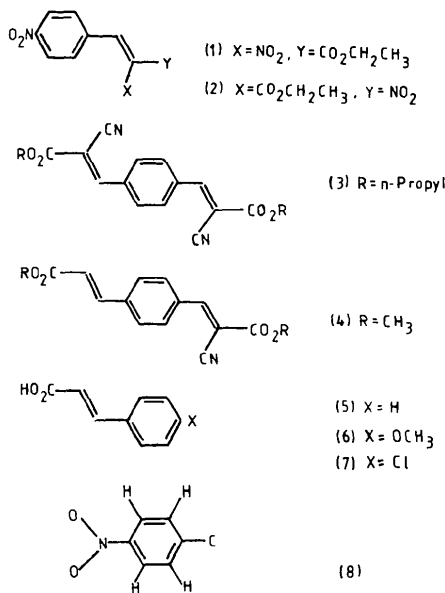*Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD, England*

Abstract. $C_{11}H_{10}N_2O_6$, $M_r = 266·1$, triclinic, $P\bar{1}$, $a = 7·803$ (4), $b = 7·860$ (5), $c = 10·961$ (5) Å, $\alpha = 77·19$ (4), $\beta = 82·16$ (4), $\gamma = 68·89$ (5)°, $U = 610·35$ Å^3, $Z = 2$, $D_c = 1·45$ Mg m^{-3}, $\mu = 0·13$ mm^{-1} (Mo $K\alpha$ radiation), $R = 0·049$ for 1558 observed reflections. The two olefinic C atoms and the attached N and carbonyl group all lie in one plane, to which the olefinic nitro group and benzene ring make angles of 80·5 (5) and 9·3 (5)° respectively. The aromatic nitro group is twisted out of the plane of the benzene ring by 20·2 (4)°.

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Introduction. The title compound (1), provided by Dr P. G. Taylor, was obtained along with its stereoisomer (2) and two trace products from the nitration of ethyl 4-nitrocinnamate with a 40:60 mixture of nitric and sulphuric acids (Moodie, Schofield, Taylor & Baillie, 1981). However, the assignment of the higher-melting-point isomer (382–384 K) as (1) rather than (2) was based only on a tentative correlation of the olefinic nitro group's IR stretching frequency. Since the position is further confused by the presence of a second nitro group, the crystal structure determination of the higher-melting isomer was undertaken.

(1) X=NO$_2$, Y=CO$_2$CH$_2$CH$_3$

(2) X=CO$_2$CH$_2$CH$_3$, Y=NO$_2$

(3) R=n-Propyl

(4) R=CH$_3$

(5) X=H

(6) X=OCH$_3$

(7) X=Cl

(8)

Oscillation and Weissenberg photographs showed the crystal system to be triclinic with two molecules per unit cell. Accurate cell dimensions were determined on an Enraf–Nonius CAD-4 four-circle diffractometer and intensity data collected using Mo $K\alpha$ radiation out to $2\theta = 58°$ by $\omega/2\theta$ scans with standard reflections checked hourly. After the merging of equivalent reflections, 2680 structure amplitudes were derived. The space group $P\bar{1}$ was assumed from the Wilson statistics. The structure was solved with *MULTAN* 77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977). A starting set of seven hand-picked reflections was used after the program had failed to solve the structure automatically. The structure was refined by full-matrix least squares, with isotropic temperature factors, using the 1558 reflections with $I \geq 3\sigma(I)$. The H atoms were then placed by calculation and assigned an isotropic temperature factor of 0·085 Å^2 and were not included in further refinement which now included anisotropic temperature factors for all the other atoms. Weights were computed from the Chebyshev series $w = [1807t_0\ (x) + 2497t_1\ (x) + 766·4t_2\ (x) + 39·58t_3 \times (x)]^{-1}$ where $x = F_o/F_{max}$ (Rollett, 1965) and the final

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* (Å^2) *for* (1) *with e.s.d.'s in parentheses*

	x	y	z	B_{eq}*
O(1)	1·1583 (4)	0·0454 (4)	0·4126 (2)	5·7
O(2)	1·3533 (3)	0·0298 (3)	0·2531 (2)	4·5
O(3)	0·7205 (3)	0·5687 (3)	−0·2109 (2)	5·1
O(4)	0·8268 (3)	0·3219 (3)	−0·2927 (2)	4·8
O(5)	0·3019 (3)	0·3099 (4)	−0·1497 (2)	5·1
O(6)	0·4238 (3)	0·4519 (3)	−0·3210 (2)	4·2
N(1)	1·1966 (3)	0·0607 (3)	0·3006 (2)	3·8
N(2)	0·7226 (3)	0·4163 (3)	−0·2211 (2)	3·5
C(1)	0·7693 (3)	0·2186 (3)	0·0560 (2)	3·3
C(2)	0·9384 (4)	0·2408 (4)	0·0125 (2)	3·9
C(3)	1·0764 (4)	0·1908 (4)	0·0927 (3)	3·8
C(4)	1·0454 (3)	0·1210 (3)	0·2169 (2)	3·2
C(5)	0·8802 (4)	0·0992 (4)	0·2648 (2)	3·7
C(6)	0·7434 (4)	0·1472 (4)	0·1832 (2)	3·5
C(7)	0·6159 (4)	0·2595 (4)	−0·0226 (2)	3·7
C(8)	0·5889 (4)	0·3414 (4)	−0·1413 (2)	3·5
C(9)	0·4219 (4)	0·3646 (4)	−0·2036 (3)	3·9
C(10)	0·2670 (5)	0·4810 (5)	−0·3934 (3)	4·9
C(11)	0·2995 (6)	0·3165 (5)	−0·4494 (4)	6·1

$$* B_{eq} = 8\pi^2\,(U_{11}\,U_{22}\,U_{33})^{1/3}.$$

Table 2. *Interatomic distances* (Å) *with e.s.d.'s in parentheses*

O(1)–N(1)	1·213 (3)	C(1)–C(6)	1·399 (3)
O(2)–N(1)	1·222 (3)	C(1)–C(7)	1·469 (4)
O(3)–N(2)	1·221 (3)	C(2)–C(3)	1·374 (4)
O(4)–N(2)	1·216 (3)	C(3)–C(4)	1·374 (4)
O(5)–C(9)	1·199 (3)	C(4)–C(5)	1·379 (3)
O(6)–C(9)	1·318 (3)	C(5)–C(6)	1·379 (4)
O(6)–C(10)	1·470 (3)	C(7)–C(8)	1·326 (4)
N(1)–C(4)	1·469 (3)	C(8)–C(9)	1·488 (4)
N(2)–C(8)	1·472 (3)	C(10)–C(11)	1·479 (5)
C(1)–C(2)	1·398 (4)		

Table 3. *Bond angles* (°) *with e.s.d.'s in parentheses*

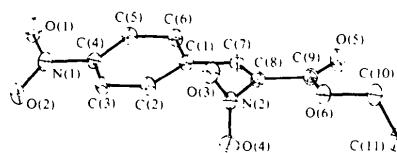|			
C(9)–O(6)–C(10)	117·3 (2)	N(1)–C(4)–C(5)	118·9 (2)
O(1)–N(1)–O(2)	124·0 (2)	C(3)–C(4)–C(5)	122·5 (2)
O(1)–N(1)–C(4)	118·0 (2)	C(4)–C(5)–C(6)	117·9 (2)
O(2)–N(1)–C(4)	118·0 (2)	C(1)–C(6)–C(5)	121·4 (2)
O(3)–N(2)–O(4)	124·8 (2)	C(1)–C(7)–C(8)	131·9 (2)
O(3)–N(2)–C(8)	117·8 (2)	N(2)–C(8)–C(7)	122·2 (2)
O(4)–N(2)–C(8)	117·5 (2)	N(2)–C(8)–C(9)	115·1 (2)
C(2)–C(1)–C(6)	118·4 (2)	C(7)–C(8)–C(9)	122·7 (2)
C(2)–C(1)–C(7)	125·1 (2)	O(5)–C(9)–O(6)	125·8 (3)
C(6)–C(1)–C(7)	116·5 (2)	O(5)–C(9)–C(8)	122·2 (3)
C(1)–C(2)–C(3)	120·6 (2)	O(6)–C(9)–C(8)	112·0 (2)
C(2)–C(3)–C(4)	119·1 (2)	O(6)–C(10)–C(11)	110·0 (3)
N(1)–C(4)–C(3)	118·6 (2)		

Fig. 1. The structure of (1) with thermal ellipsoids drawn at the 50% probability level.

R value was 0·049. Data reduction, structure refinement and geometry calculations were performed on the Oxford University ICL 1906A computer with CRYSTALS (Carruthers, 1978). Final atomic coordinates with B_{eq} values, bond lengths and bond angles are presented in Tables 1–3.* A view of the molecule is shown in Fig. 1.

Discussion. The crystal structure confirmed the assignment of the higher-melting isomer as (1). The olefinic C(7) and C(8), the attached N atom and carbonyl group all lie in one plane (plane 1). The plane of the aliphatic nitro group lies at 80·5 (5)° to this plane and the best plane through the benzene ring lies at 9·3 (5)° to it so that the ortho H(21) and O(4) lie on the same side of plane (1) and the small tilt of the nitro group away from orthogonality with this plane maximizes the distance between these two atoms. The H atom in its calculated position lies 2·4 Å from N(2) similar to the analogous distances in the cyanocinnamates (3) (Nakanishi & Sasada, 1978) and (4) (Nakanishi, Ueno & Sasada, 1976). The interaction of H(21) and N(2) is also reduced by a widening of the angles C(1)–C(7)–C(8) and C(2)–C(1)–C(7) by 4·9 and 2·2° compared with the averaged data for the α-unsubstituted cinnamic acids (5), (6) (Bryan & Freyberg, 1975) and (7) Glusker, Zacharias & Carrell, 1975) [ranges: C(1)–C(7)–C(8) 126·3 (3)–127·6 (2)°; C(2)–C(1)–C(7) 122·6 (3)–123·2 (2)°] with a consequent reduction of C(6)–C(1)–C(7) to 116·5 (2)°. The α-cyanocinnamates (3) and (4) show similar effects though in the latter compound only C(1)–C(7)–C(10) is widened. The lengths of

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and the results of mean-plane calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36759 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

C(1)–C(7) and the olefinic bond C(7)–C(8) are very similar to the equivalent bonds in cinnamic acid (5) [1·467 (4) and 1·322 (4) Å respectively] (Bryan & Freyberg, 1975), but the double bond is shorter than that in the cyano ester (3) [1·341 (3) Å] which is consistent with conjugation of the cyano group with the double bond while the similarly positioned nitro group cannot conjugate. The molecules of (1) are stacked along the b axis (Fig. 2).

The plane of the aromatic nitro group lies at an angle of 20·2 (4)° to the best plane through the benzene ring. A search of the Cambridge Crystallographic Database (Allen et al., 1979) for p-nitrobenzene derivatives using the fragment (8) revealed that only three out of the 78 compounds found had a larger value for this angle. There does not appear to be a clear correlation of the size of this angle with the electronic character of the para substituent (e.g. for p-nitrobenzoates the angle can vary from 1·8 to 21·0°); however, the larger angles do occur when the para substituent is strongly electron withdrawing. It has been shown that only a small amount of energy is required to rotate the nitro group 18° out of the plane of the benzene ring (Dorset, Hybl & Ammon, 1972), so packing forces may control the size of this angle in many cases.

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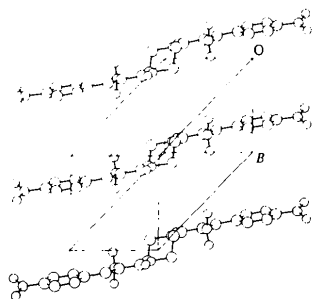Fig. 2. Packing diagram showing stacking along the y axis.