

Acta Cryst. (1975). B31, 1963Methyl 4-Hydroxy-3-nitro-*trans*-cinnamate

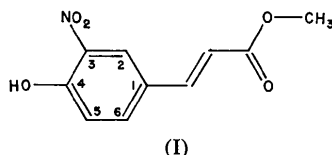
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Abstract. C₁₀H₉NO₅, F.W. 223.2, monoclinic, *P*2₁/*c*, *a* = 3.873(4), *b* = 21.34(2), *c* = 12.15(1) Å, β = 90.9(1)° (20°C), *D*_m = 1.48 g cm⁻³, *Z* = 4, *D*_x = 1.477 g cm⁻³. The molecule is nearly planar, with an intramolecular hydrogen bond joining the hydroxyl group to one O atom of the nitro group. The C–C double bond lies to the same side of the 1,4 axis of the molecule as the nitro group; the conformation about the acryloyl single bond is *s-cis*.

Introduction. Certain substrates of chymotrypsin have resonance Raman spectra which are sensitive to the binding reaction (Carey & Schneider, 1974, 1975). The title compound (I) is such a compound; the crystal structure analysis was undertaken in order to provide conformational data to assist in studies of the reaction mechanism.



The material crystallizes from methanol as orange needles bounded by (100) and (011); needles are often terminated by (102), which is a good cleavage plane. The space group was determined from single-crystal photographs. The specimen used for intensity measurements was a fragment of a needle, 0.15 × 0.17 × 0.4 mm. This was mounted about *a* and the intensities of the 1704 independent reflexions within the limiting sphere 2θ = 130° were measured with a Picker four-circle diffractometer, Ni-filtered Cu Kα radiation, and a scintillation counter. The θ-2θ scan mode was used, with scans of 2° for 2θ < 100°, and 3° otherwise. The scanning rate was 2° min⁻¹, and background counts were accumulated for 20 s at the beginning and end of each scan. 413 reflexions were considered to be unobserved, as their net intensities were less than either 50 counts or 10% of the corresponding background intensity. No correction was made for absorption (μ = 11.9 cm⁻¹).

The structure was determined by symbolic addition procedures. The application was not straightforward, providing yet another example of an *E* map which mimics a disordered structure; two half-weight mole-

Table 1. Final parameters

Quantities given are: for non-hydrogen atoms, fractional coordinates × 10⁵; *U*₁₁ × 10⁴ Å² T.F. = exp [−2π²(*U*₁₁*a*²*h*² + ... + 2*U*₁₂*a*^{*}*b*^{*}*h**k* + ...)]. For hydrogen atoms, fractional coordinates × 10³; Debye–Waller factors *B*, in Å². E.s.d.'s are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
C(1)	−7052 (61)	66105 (10)	48483 (19)	457 (13)	369 (12)	491 (12)	7 (9)	−8 (10)	51 (9)
C(2)	−13599 (62)	72002 (10)	52748 (18)	519 (13)	399 (12)	419 (11)	8 (9)	61 (10)	12 (10)
C(3)	−4366 (62)	77352 (10)	46990 (18)	508 (13)	353 (12)	458 (12)	−2 (9)	35 (10)	39 (10)
C(4)	12268 (63)	76953 (11)	36857 (19)	512 (14)	440 (12)	483 (12)	80 (10)	50 (11)	8 (10)
C(5)	18326 (70)	71053 (12)	32630 (20)	629 (15)	517 (14)	449 (12)	11 (11)	119 (11)	53 (12)
C(6)	9225 (67)	65781 (11)	38310 (19)	572 (15)	407 (12)	500 (13)	−32 (10)	46 (11)	61 (10)
N(7)	−12533 (64)	83399 (9)	51739 (18)	746 (15)	384 (9)	565 (12)	15 (9)	82 (10)	34 (9)
O(8)	−29411 (70)	83592 (9)	60068 (18)	1252 (19)	466 (9)	744 (13)	−56 (9)	399 (13)	87 (11)
O(9)	−2261 (69)	88181 (8)	47181 (18)	1209 (18)	360 (9)	852 (13)	60 (9)	261 (13)	−19 (10)
O(10)	22868 (60)	81887 (8)	30868 (16)	937 (15)	491 (9)	661 (11)	170 (9)	258 (10)	−15 (9)
C(11)	−16550 (66)	60296 (10)	54161 (20)	576 (15)	350 (12)	502 (13)	−40 (9)	41 (11)	46 (10)
C(12)	−32423 (66)	59864 (11)	63556 (20)	581 (15)	366 (12)	532 (13)	−10 (10)	109 (12)	23 (10)
C(13)	−40226 (67)	53754 (11)	68553 (20)	567 (14)	372 (12)	511 (13)	11 (10)	8 (11)	−5 (10)
O(14)	−55785 (52)	54479 (8)	78257 (16)	828 (13)	428 (9)	563 (10)	61 (7)	156 (9)	−57 (8)
O(15)	−33486 (65)	48748 (8)	64879 (17)	1136 (17)	385 (9)	746 (12)	10 (8)	256 (12)	66 (9)
C(16)	−64320 (87)	48811 (14)	84081 (26)	780 (20)	618 (16)	742 (19)	227 (14)	125 (15)	−79 (14)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(2)	−237 (7)	726 (1)	594 (2)	3.5 (0.5)	H(12)	−416 (8)	635 (1)	678 (2)	5.2 (0.6)
H(5)	299 (7)	709 (1)	259 (2)	4.6 (0.6)	H(16,1)	−447 (10)	463 (2)	850 (3)	7.2 (0.8)
H(6)	115 (8)	616 (1)	354 (2)	5.1 (0.6)	H(16,2)	−758 (12)	501 (2)	906 (4)	8.8 (1.0)
H(10)	176 (11)	853 (2)	350 (3)	7.8 (0.9)	H(16,3)	−764 (10)	458 (2)	793 (3)	7.0 (0.8)
H(11)	−115 (7)	564 (1)	504 (2)	4.1 (0.5)					

cules appeared to be separated by one of the multiply-occurring interatomic vectors, and the correct solution proved to be the average of these (Bürgi & Dunitz, 1971). Refinement was by the block-diagonal least-squares method; the quantity minimized was $\sum w\Delta F^2$, where $w = w_1 w_2$, with $w_1 = F_o/7$ for $F_o < 7$, $= 7/F_o$ otherwise, and $w_2 = \sin^2 \theta/0.35$ for $\sin^2 \theta < 0.35$, $= 1$ otherwise.

This weighting scheme was found to be effective in removing systematic dependence of the weighted residual on F_o and θ . The H atoms were included with initial positions either determined from a ΔF synthesis (methyl and hydroxyl groups) or assigned on reasonable chemical grounds. On termination of refinement R (for observed reflexions only) was 0.048.* On the last cycle the maximum coordinate shift of a non-hydrogen atom was 40% of the corresponding e.s.d. (12% if the methyl C atom is excepted). The final atomic parameters are given in Table 1.

The computer programs used were those of Ahmed, Hall, Pippy & Huber (1966). Scattering factors were taken from Stewart, Davidson & Simpson (1965) for H, and from Hanson, Herman, Lea & Skillman (1964).

Table 2. Bond lengths (Å) and angles (°)

C(1)—C(2)	1.386 (3)	C(1)—C(2)—C(3)	120.5 (2)
C(2)—C(3)	1.388 (3)	C(2)—C(3)—C(4)	121.2 (2)
C(3)—C(4)	1.401 (3)	C(3)—C(4)—C(5)	117.7 (2)
C(4)—C(5)	1.381 (3)	C(4)—C(5)—C(6)	121.0 (2)
C(5)—C(6)	1.369 (3)	C(5)—C(6)—C(1)	121.9 (2)
C(6)—C(1)	1.398 (3)	C(6)—C(1)—C(2)	117.6 (2)
C(3)—N(7)	1.450 (3)	C(2)—C(3)—N(7)	118.1 (2)
N(7)—O(8)	1.214 (3)	C(4)—C(3)—N(7)	120.6 (2)
N(7)—O(9)	1.230 (3)	C(3)—N(7)—O(8)	119.0 (2)
C(4)—O(10)	1.348 (3)	C(3)—N(7)—O(9)	119.0 (2)
C(1)—C(11)	1.468 (3)	C(3)—C(4)—O(10)	125.1 (2)
C(11)—C(12)	1.308 (4)	C(2)—C(1)—C(11)	122.8 (2)
C(1)—C(13)	1.471 (3)	C(1)—C(11)—C(12)	126.4 (2)
C(13)—O(14)	1.341 (3)	C(11)—C(12)—C(13)	121.6 (2)
O(14)—C(16)	1.442 (4)	C(12)—C(13)—O(14)	111.0 (2)
C(13)—O(15)	1.188 (3)	C(12)—C(13)—O(15)	126.4 (2)
O(10)···O(9)	2.596 (3)	C(13)—O(14)—C(16)	116.4 (2)

Table 3. Distances (Å × 10³) of some atoms from specified planes

(102) plane containing (0, 0, $\frac{1}{2}$): C(1) -327; C(2) -263; C(3) -337; C(4) -454; C(5) -532; C(6) -459; N(7) -294; O(8) -301; O(9) -256; O(10) -500; C(11) -267; C(12) -172; C(13) -101; O(14) 24; O(15) -121; C(16) 125.

Mean plane of non-hydrogen atoms: C(1) 4; C(2) -14; C(3) -7; C(4) -3; C(5) 29; C(6) 22; N(7) 1; O(8) 107; O(9) -93; O(10) -29; C(11) 10; C(12) 22; C(13) 9; O(14) -6; O(15) -11; C(16) -41.

Mean plane of C(1)···C(6): C(1) -1; C(2) -1; C(3) 6; C(4) -8; C(5) 6; C(6) -1; N(7) 35; O(8) 157; O(9) -59; O(10) -35; C(11) 4.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30984 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion. The bond lengths and angles are consistent with expectation, and are listed in Table 2. The molecule is essentially planar (Table 3); the nitro group is bent and twisted out of the ring plane by about 6°, but otherwise no non-hydrogen atom lies more than 0.04 Å from the mean plane of the molecule. The position of the hydroxyl H atom is consistent with a bond to one O atom of the nitro group. The conformation is as depicted above and in Fig. 1. The structure can be described as consisting of sheets of molecules lying close to the (102) planes. Within a given sheet no non-hydrogen atom lies more than 0.53 Å from the corresponding plane, and the average distance is 0.24 Å. (The distance between adjacent planes is 3.24 Å.)

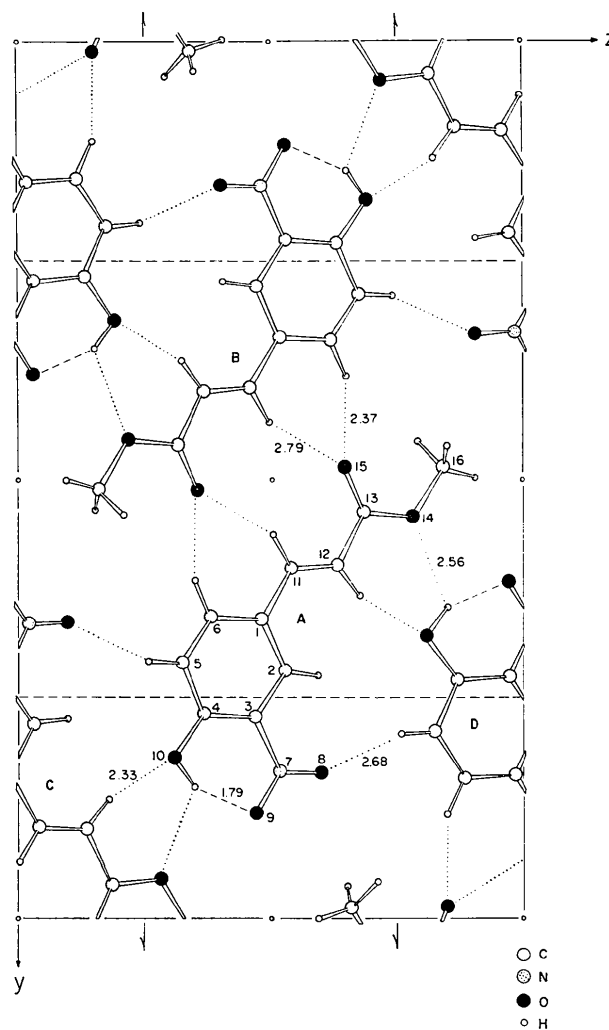


Fig. 1. The structure viewed along *a*. The intramolecular O—H···O bond is shown as a dashed line, while short intermolecular O···H contacts are shown as dotted lines. The lettered molecules are related to that specified in Table 1 as follows: A: x, y, z ; B: $-x, 1-y, 1-z$; C: $1+x, 1\frac{1}{2}-y, -\frac{1}{2}+z$; D: $-1+x, 1\frac{1}{2}-y, \frac{1}{2}+z$.

This structural feature accounts for the (102) cleavage and for the great intensity of the 102 reflexion (64% of the theoretical maximum). Contact between adjacent molecules in a sheet is essentially edge-to-edge. The shortest intermolecular distances are between O and H; five such, shown in Fig. 1, range from 2.33 to 2.70 Å. One of these involves the hydroxyl H atom and can be described as a branch (albeit at 2.56 Å, a long one) of a bifurcated hydrogen bond. The others involve aromatic and ethylenic H atoms. Notwithstanding the equivocal reputation of the C-H...O bond (Donohue, 1968), it seems reasonable to describe the shorter of these interatomic vectors as weak bonds which mediate the sheet-like arrangement of the structure. It is suggested that the electron-withdrawing effect of the nitro and carbomethoxy groups is sufficient to induce significant acidic character in the H atoms involved.

Acta Cryst. (1975). B31, 1965

N-Carbomethoxyamino-3,6-dimethyl-4,5-diphenyl-2-pyridone

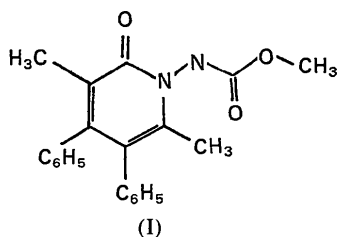
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Abstract. C₂₁H₂₀N₂O₃, M.W. 348.41, monoclinic, *C*2/*c*, *a* = 16.127 (2), *b* = 6.835 (1), *c* = 34.553 (8) Å, β = 93.25 (2)°; *U* = 3802.4 (1.3) Å³; *d*_{meas} = 1.21, *d*_{calc} = 1.217 g cm⁻³, *Z* = 8. The final *R* was 0.040 for 1927 reflections used in the analysis. There is significant delocalization in the pyridone ring which is not exactly planar. A very strong N-H...O hydrogen bond between two molecules related by a center produces dimer-like units separated by normal von der Waals forces.

Introduction. Crystals of *N*-carbomethoxyamino-3,6-dimethyl-4,5-diphenyl-2-pyridone (I) were supplied by Professor D. Mackay, University of Waterloo.



Preliminary precession photographs indicated the space groups *Cc* or *C*2/*c*. Intensity statistics favored *C*2/*c*, and the choice was confirmed by the structure

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analysis. A crystal 0.30 × 0.22 × 0.19 mm was mounted on a Syntex PI diffractometer and used to determine the cell constants and the intensity measurements. The experimental details were identical with those given by Dymock & Palenik (1974). Of the 2397 reflections measured, the 1927 reflections with *I* ≥ 2.0 σ(*I*) were used in the analysis. The intensities were reduced to a set of structure amplitudes on an arbitrary scale by the application of Lorentz-polarization corrections.

The structure was solved by the symbolic addition procedure using the computer programs *FAME-MAGIC-LINK-SYMP* described by Dewar (1970). The refinement was carried out by full-matrix least-squares techniques using first isotropic and then anisotropic thermal parameters. All the hydrogen atoms were located in a difference Fourier synthesis. The hydrogen atom parameters were also refined in subsequent least-squares calculations using a block approximation. The final *R* (the usual residual) was 0.040 for the 1927 reflections used in the analysis.* The final parameters are given in Tables 1 and 2.

* Tables of observed and calculated structure factors and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30999 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.