

(E)-1-(4'-HYDROXY-3'-METHOXYPHENYL)-2-NITROPROPENE, C₁₀H₁₁NO₄

Volker Zabel, William H. Watson*, Bruce K. Cassels**

and David A. Langs***

FASTBIOS Laboratory, Department of Chemistry, Texas Christian University, Fort Worth, TX, 76129, U.S.A.; **Universidad Tecnica del Estado, Facultad de Ciencia, Departamento de Quimica, Santiago, Chile; ***Medical Foundation of Buffalo, 73 High Street, Buffalo, NY

Cinnamic acid, coumaric acid and their derivatives have been investigated by X-ray diffraction techniques for a variety of reasons. p-Chloro-trans-cinnamic acid undergoes a photochemical reaction in the solid state which is related to the proximity of the side chain double bonds (Glusker, Zacharias & Carrell, 1975). p-Methoxy-trans-cinnamic acid and related derivatives exhibit thermotropism (Bryan & Freyberg, 1975). The p-chloro and p-methoxy compounds are essentially planar with torsion or interplanar angles of 0.9° and 4.6°. 2-Coumaric acid (Raghunathan & Pattabhi, 1979) and p-coumaric acid (Utsumi, Fujii, Irie, Furusaki & Nitta, 1970) exhibit interplanar angles of 4.8° and 5.0°, which indicate only weak steric interactions; however, the interplanar angles in β -chloro-trans-cinnamic acid, β -chloro-cis-cinnamic acid and β -methyl-cis-cinnamic acid are 11.7°, 65.4° and 83°, respec-

tively (Filippakis, Leiserowitz, Rabinovich & Schmidt, 1972). Although increased steric interactions are present in these compounds, the large departures from planarity can be attributed to additional intermolecular interactions once the energy of conjugation has been lost.

(E)-1-(4'-Hydroxy-3'-methoxyphenyl)-2-nitropropene is analogous to the cinnamic and coumaric acids and in addition is of interest because of the relationship with several antitumor arylnitroalkenes and naturally occurring aristolochic acids.

A crystal of dimensions 0.6 , 0.15 , 0.3 mm was used to collect all X-ray data on a Syntex P2₁ diffractometer. Room-temperature lattice parameters were refined by a least-squares procedure utilizing 15 reflexions whose angles were measured by a centering routine associated with the diffractometer. No systematic absences were observed and statistics were consistent with space group P $\bar{1}$.

Crystal data: C₁₀ H₁₁ NO₄, MW 209.20, a = 7.105(1), b = 8.238(2), c = 8.476(2) Å, α = 93.87(2), β = 94.28(2), γ = 90.83(2)^o, V = 493.5(2) Å³, Z = 2, d_c = 1.408 gcm⁻³.

Intensity data were collected by the θ:2θ scanning technique using a variable scan speed, a graphite monochromator and CuKα radiation (λ = 1.54178 Å). 1337 independent reflexions were measured and 1265 had intensities greater than 2 σ(I). A periodically monitored reflexion showed no significant change in intensity. Lorentz and polarization corrections were applied, but no absorption corrections were

made. The structure was solved initially in space group P1 using QTAN (Langs & DeTitta, 1975) and transformed to $P\bar{1}$. All atoms were found in the first E map and the model was refined isotropically by least-squares procedures to an R factor of 12.3% and anisotropically to 10.3%. Hydrogen atoms were located in a difference Fourier map and full-matrix refinement with hydrogen atom thermal parameters isotropic led to a final R of 5.8% where $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. The function minimized in the refinement was $\Sigma \omega (|F_o| - |F_c|)^2$ where $\omega = 1 / \sigma(I)$ was determined from counting statistics.

Table I. Positional parameters $\times 10^4$ ($H \times 10^3$).

| atom | x/a | y/b | z/c |
|--------|----------|---------|----------|
| C(1) | 0669(4) | 4334(3) | 3000(3) |
| C(2) | 1083(3) | 3043(2) | 1798(2) |
| C(3) | 2549(3) | 2038(3) | 1756(3) |
| C(1') | 4140(3) | 1899(2) | 2939(3) |
| C(2') | 4092(3) | 2402(2) | 4553(3) |
| C(3') | 5651(3) | 2243(2) | 5581(3) |
| O(3') | 5781(2) | 2678(2) | 7176(2) |
| C(4') | 7292(3) | 1571(2) | 5046(3) |
| O(4') | 8840(2) | 1420(2) | 6053(3) |
| C(5') | 7352(3) | 1053(3) | 3471(3) |
| C(6') | 5788(3) | 1203(3) | 2447(3) |
| C(7') | 4273(4) | 3531(4) | 7818(3) |
| N(1) | -0305(3) | 2872(2) | 0423(2) |
| O(2) | -1648(2) | 3780(3) | 0405(2) |
| O(3) | -0057(3) | 1859(3) | -0677(3) |
| H(1a) | 200(5) | 479(4) | 356(4) |
| H(1b) | 015(6) | 553(7) | 250(6) |
| H(1c) | -005(4) | 398(4) | 372(4) |
| H(3) | 264(4) | 128(4) | 080(4) |
| H(2') | 298(4) | 274(3) | 494(3) |
| H(4') | 858(4) | 159(3) | 681(4) |
| H(5') | 850(4) | 048(3) | 303(3) |
| H(6') | 584(4) | 082(4) | 134(4) |
| H(7a') | 455(5) | 366(5) | 892(5) |
| H(7b') | 295(6) | 292(5) | 760(5) |
| H(7c') | 407(4) | 456(4) | 733(4) |

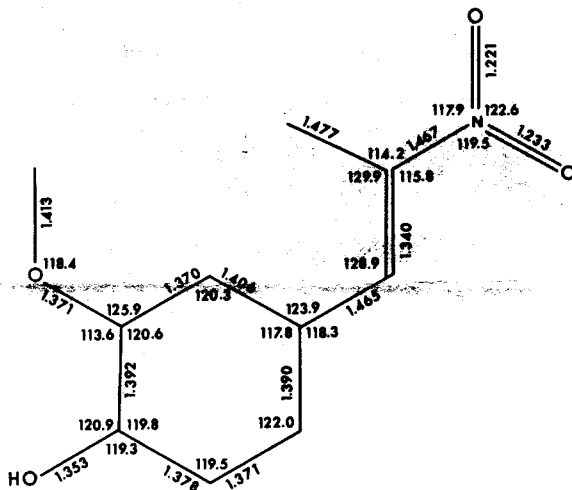


Figure 1. Bond distances and valence angles. The corresponding esd's do not exceed 0.003 Å or 0.2° except for the C(3') methoxy group.

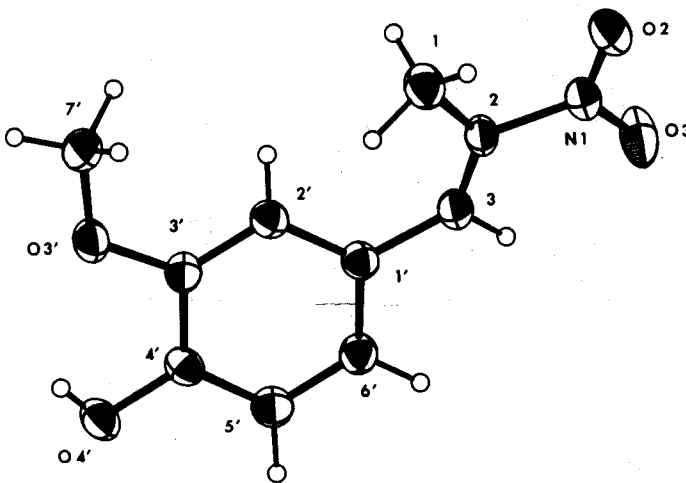


Figure 2. ORTEP drawing. Thermal ellipsoids shown at 35% probability level while hydrogen atoms are presented as arbitrary sized spheres.

During the final cycle all shifts in parameters were less than 0.4σ and a final difference map showed no peak larger than $0.3 \text{ e}/\text{A}^3$. Atomic scattering factors were taken from International Tables for X-ray Crystallography (1974). Atomic positional parameters are given in Table 1 while interatomic distances and valence angles are presented in Figure 1.

Discussion: Figure 2 is an ORTEP drawing (Johnson, 1965) of the title compound. A least-squares plane fitted to the phenyl ring and attached atoms shows maximum deviations of 0.02 \AA by C(6') and O(4'). The C(7') methyl group lies 0.12 \AA out of the plane. A least squares plane fitted to the side chain atoms and C(1') shows a maximum deviation of 0.01 \AA from planarity. The molecule exhibits an interplanar angle of 23.7 and a C(2')-C(1')-C(3)-C(2) torsion angle of $22.8(4)^\circ$. In order to minimize steric interactions the C(1')-C(3)-C(2) and C(1)-C(2)-C(3) valence angles expand to $128.9(2)$ and $129.9(2)$ resulting in contact distances of C(1)-C(2') = $3.185(3) \text{ \AA}$, H(1a)-H(2') = $2.22(4) \text{ \AA}$, H(1c)-H(2') = $2.58(3) \text{ \AA}$, C(1)-H(2') = $2.66(2) \text{ \AA}$ and H(6')-H(3) = $2.33(4) \text{ \AA}$. The C(3)-C(1') distance of $1.465(3) \text{ \AA}$ is shorter than the $1.486(4)$ and $1.484(4) \text{ \AA}$ values reported for β -chloro-trans-cinnamic acid and β -methyl-cis-cinnamic acid, comparable with the $1.469(4)$ and $1.459(2) \text{ \AA}$ values for β -chloro-cis-cinnamic acid and trans-cinnamic acid (Bryan & Freyberg, 1975), but longer than the $1.451(4) \text{ \AA}$ value reported for p-chloro-trans-cinnamic acid. A rough correlation

may be made between the magnitude of the interplanar angle, the degree of conjugation and the length of the C(3)-C(1') bond.

An intermolecular hydrogen bond is formed between the hydroxyl hydrogen H(4') and the O(3) (1+x,y,1+z) nitro oxygen atom where $O(4')..O(3) = 2.822(3) \text{ \AA}$, $O(4')-H(4') = 0.70(3) \text{ \AA}$, $H(4')..O(3) = 2.27(3) \text{ \AA}$. The inequality in the N-O distances is consistent with the participation of one oxygen atom in hydrogen bonding.

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