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Acta Cryst. (1995). C**51**, 1364–1366

Methyl 3,5-Dinitro-*trans*-cinnamate

C. V. Krishnamohan Sharma, Kaliyamoorthy Panneerselvam and Gautam R. Desiraju

School of Chemistry, University of Hyderabad,
PO Central University, Hyderabad 500134, India

Tullio Pilati

Dipartimento di Chimica Fisica ed Elettrochimica e
Centro CNR, Universita di Milano, 20133 Milano,
Italy

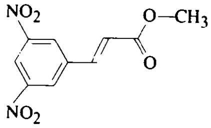
(*Received* 7 *March* 1994; *accepted* 18 *July* 1994)

Abstract

The title compound, $C_{10}H_8N_2O_6$, forms C—H···O hydrogen-bonded inversion dimers in the crystal with a calculated (AM1) energy of -8.2 kcal mol^{-1} (1 cal = 4.184 J). These dimers in turn form a planar sheet structure which is stacked along the [100] direction.

Comment

The C—H···O hydrogen bonds were found to be structure determining in the crystal structure of 3,5-dinitrocinnamic acid, (2), wherein the carboxyl groups were related by the uncommon twofold axis rather than the expected inversion centre (Desiraju & Sharma, 1991). Furthermore, one of the nitro groups in this molecule is involved in a C—H···O self-recognition motif (Sharma, Panneerselvam, Pilati & Desiraju, 1993). To further investigate the C—H···O bond-forming ability of the 3,5-dinitrocinnamyl skeleton, we undertook the structure determination of the corresponding methyl ester, (1).



(1)

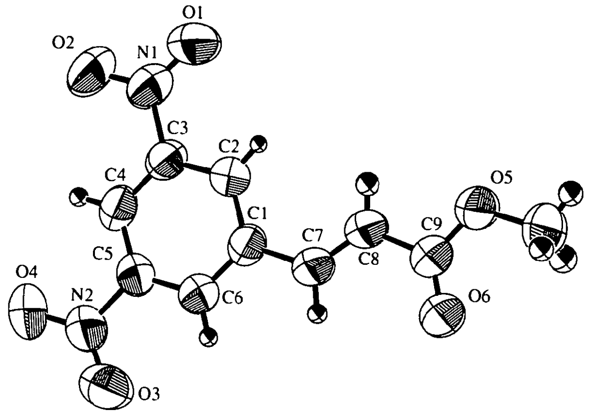


Fig. 1. An *ORTEP*II (Johnson, 1976) diagram of compound (1). Displacement ellipsoids are plotted at the 50% probability level. For clarity, H atoms are drawn as small circles.

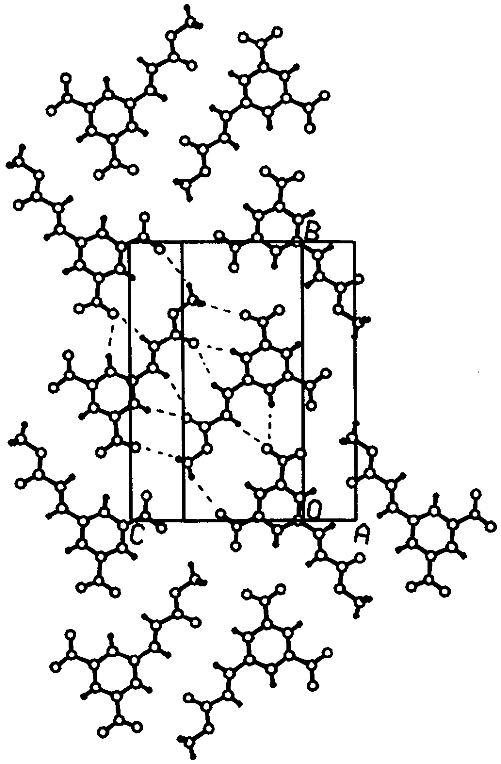


Fig. 2. The crystal structure of (1) along the [100] direction showing the planar structure.

Acta Crystallographica Section C
ISSN 0108-2701 ©1995

An *ORTEP*II (Johnson, 1976) diagram of the structure is shown in Fig. 1. The crystal structure of (1) contains an inversion dimer that is stabilized by two types of bifurcated-acceptor (Jeffrey & Saenger, 1991) C—H···O bonds (Fig. 2). The carbonyl O atom interacts with two alkene H atoms [C···O 3.285 (3) and 3.699 (3) Å, C—H···O 168 (2) and 148 (2)°], while the nitro O atom, O3, interacts with two methyl H atoms, albeit weakly [C···O 3.247 (5) Å, C—H···O 96 (3) and 117 (3)°]. These dimer units in turn form C—H···O bonds with surrounding dimers through other lateral C—H···O interactions leading to a planar structure along the [100] direction. The crystal structure of (1) is, in effect, two-dimensional compared to that of the parent acid, (2), which is three-dimensional. The strength of the inversion dimer was approximated using AM1 molecular-orbital calculations and found to be -8.2 kcal mol^{-1} (Turi & Dannenberg, 1993).

Experimental

The title compound was prepared by reacting 3,5-nitrocinnamic acid with diazomethane in dry ether.

Crystal data

$C_{10}H_8N_2O_6$
$M_r = 252.18$
Monoclinic
$P2_1/n$
$a = 4.842\ (2)$ Å
$b = 16.848\ (4)$ Å
$c = 13.489\ (3)$ Å
$\beta = 90.56\ (2)°$
$V = 1100.4\ (6)$ Å^3
$Z = 4$
$D_x = 1.522$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 10$–$20°$
$\mu = 0.129$ mm^{-1}
$T = 293\ (2)$ K
Needle
0.33 × 0.20 × 0.10 mm
Pale yellow

Data collection

Nicolet Siemens *P*3 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1932 measured reflections
1932 independent reflections
1136 observed reflections [$I > 2\sigma(I)$]

$\theta_{\max} = 24.97°$
$h = 0 \rightarrow 5$
$k = 0 \rightarrow 20$
$l = -15 \rightarrow 16$
3 standard reflections monitored every 200 reflections
frequency: 100 min
intensity decay: 2.5%

Refinement

Refinement on F^2
$R(F) = 0.0476$
$wR(F^2) = 0.1295$
$S = 0.998$
1932 reflections
195 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0695P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.247$ e Å^{-3}
$\Delta\rho_{\min} = -0.176$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1	0.4867 (5)	0.00069 (14)	0.1782 (2)	0.0519 (6)
C2	0.2879 (5)	−0.0321 (2)	0.2409 (2)	0.0557 (6)
C3	0.1450 (4)	0.01628 (14)	0.3045 (2)	0.0542 (6)
C4	0.1867 (5)	0.0964 (2)	0.3094 (2)	0.0582 (7)
C5	0.3844 (5)	0.12769 (14)	0.2486 (2)	0.0576 (6)
C6	0.5339 (5)	0.08187 (15)	0.1836 (2)	0.0568 (6)
C7	0.6499 (5)	−0.0470 (2)	0.1086 (2)	0.0563 (6)
C8	0.6507 (6)	−0.1237 (2)	0.0999 (2)	0.0664 (8)
C9	0.8277 (5)	−0.1658 (2)	0.0291 (2)	0.0624 (7)
C10	0.9649 (10)	−0.2915 (3)	−0.0301 (3)	0.0898 (11)
N1	−0.0642 (4)	−0.0193 (2)	0.3690 (2)	0.0684 (6)
N2	0.4429 (5)	0.21349 (13)	0.2529 (2)	0.0740 (7)
O1	−0.0855 (5)	−0.09054 (14)	0.3697 (2)	0.1015 (8)
O2	−0.2077 (4)	0.02533 (12)	0.4179 (2)	0.0849 (6)
O3	0.6481 (6)	0.23766 (12)	0.2135 (2)	0.1272 (11)
O4	0.2862 (5)	0.25531 (11)	0.2984 (2)	0.0991 (8)
O5	0.7900 (4)	−0.24360 (11)	0.03205 (14)	0.0806 (6)
O6	0.9876 (4)	−0.13403 (11)	−0.02541 (15)	0.0859 (7)

Table 2. *Selected geometric parameters* (Å, °)

C1—C6	1.388 (3)	C7—C8	1.298 (3)
C1—C2	1.401 (3)	C8—C9	1.472 (3)
C1—C7	1.472 (3)	C9—O6	1.199 (3)
C2—C3	1.376 (3)	C9—O5	1.324 (3)
C3—C4	1.366 (3)	C10—O5	1.444 (4)
C3—N1	1.470 (3)	N1—O1	1.204 (3)
C4—C5	1.372 (3)	N1—O2	1.221 (3)
C5—C6	1.378 (3)	N2—O3	1.202 (3)
C5—N2	1.474 (3)	N2—O4	1.207 (3)
C6—C1—C2	118.1 (2)	C8—C7—C1	127.2 (2)
C6—C1—C7	118.9 (2)	C7—C8—C9	122.7 (3)
C2—C1—C7	123.0 (2)	O6—C9—O5	123.4 (2)
C3—C2—C1	119.7 (2)	O6—C9—C8	124.5 (3)
C4—C3—C2	122.8 (2)	O5—C9—C8	112.1 (2)
C4—C3—N1	118.5 (2)	O1—N1—O2	124.1 (2)
C2—C3—N1	118.8 (2)	O1—N1—C3	118.1 (2)
C3—C4—C5	117.1 (2)	O2—N1—C3	117.8 (2)
C4—C5—C6	122.6 (2)	O3—N2—O4	123.6 (2)
C4—C5—N2	119.2 (2)	O3—N2—C5	118.3 (2)
C6—C5—N2	118.2 (2)	O4—N2—C5	118.1 (2)
C5—C6—C1	119.9 (2)	C9—O5—C10	117.0 (3)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O4$^{\rm i}$	0.87 (2)	2.78 (2)	3.637 (3)	168 (2)
C6—H6···O6$^{\rm ii}$	0.86 (2)	2.42 (3)	3.285 (3)	168 (2)
C7—H7···O6$^{\rm ii}$	0.94 (3)	2.87 (3)	3.699 (3)	148 (2)
C8—H8···O4$^{\rm i}$	0.89 (3)	2.38 (3)	3.251 (4)	167 (3)
C10—H101···O2$^{\rm i}$	0.87 (4)	2.84 (4)	3.662 (5)	157 (3)
C10—H102···O3$^{\rm ii}$	0.95 (4)	2.70 (4)	3.247 (5)	117 (3)
C10—H103···O3$^{\rm ii}$	0.95 (4)	3.01 (4)	3.247 (5)	96 (3)
C10—H102···O4$^{\rm iii}$	0.95 (4)	2.91 (4)	3.854 (6)	171 (3)
C10—H103···O4$^{\rm iv}$	0.95 (4)	2.94 (4)	3.431 (5)	114 (3)

Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (ii) $2 - x, -y, -z$; (iii) $1 - x, -y, -z$; (iv) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

Data collection: Nicolet Siemens *P*3 diffractometer software. Cell refinement: Nicolet Siemens *P*3 diffractometer software. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *SHELXL*93.

We thank the Department of Science and Technology and the University Grants Commission, Government of India, for financial assistance.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SE1059). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 1366–1368

Construction of the Tetracyclic Skeleton of Leucothol A. 1,2,4a,5,6,7,8,9,10,10a,11,11a-Dodecahydro-11-hydroxy-11-methyl-7-phenylthiomethyl-5a*H*-5a,8-methanocyclohepta[*b*]naphthalen-10-one

George A. Kraus, Qiaogong Su and
Victor G. Young Jr

Gilman Hall, Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111, USA

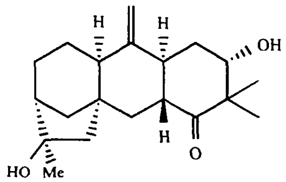
(*Received* 17 *June* 1994; *accepted* 2 *December* 1994)

Abstract

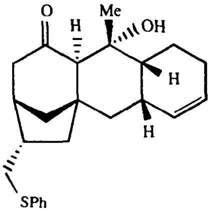
The title compound, $C_{24}H_{30}O_2S$, is a tetracyclic intermediate for the synthesis of leucothol A and the first example of an ethanoanthracene skeleton to be synthetized. The single-crystal X-ray structure of this compound is presented.

Comment

Leucothol A, (1), is a novel diterpene isolated from the leaves of *Leucothol grayana* (Hikino, Koriyama & Takemoto, 1973). Although structurally different members of this family, such as the grayanotoxins, have been synthetized previously, the ethanoanthracene skeleton has not. The significant central nervous system activity of closely related products and the novel structural elements contained within the leucothol A skeleton combine to make it a worthwhile synthetic objective. We have recently completed the first synthetic pathway leading to an ethanoanthracene product. The title compound, (2), is formed in a seven-step synthetic sequence that is initiated by a novel bridgehead connection. The details of the synthesis are published elsewhere (Kraus & Su, 1994).



(1)



(2)

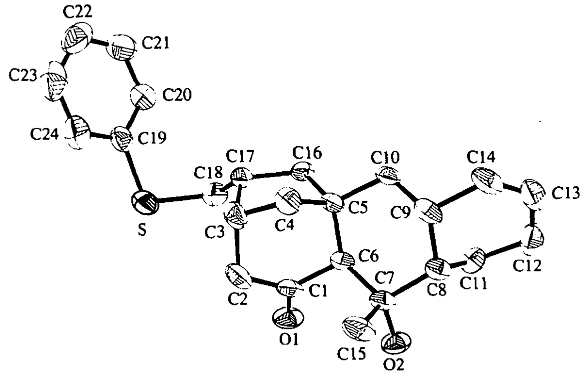


Fig. 1. The structure of the title compound showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

Crystal data

$C_{24}H_{30}O_2S$
$M_r = 382.54$
Monoclinic
$P2_1/c$
$a = 5.976\,(1)$ Å
$b = 13.146\,(1)$ Å
$c = 25.883\,(3)$ Å
$\beta = 93.84\,(1)^\circ$
$V = 2028.8\,(4)$ Å^3
$Z = 4$
$D_x = 1.252$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 20.9–26.9^\circ$
$\mu = 1.529$ mm^{-1}
$T = 213\,(1)$ K
Monoclinic
0.50 × 0.45 × 0.15 mm
Colorless

Acta Crystallographica Section C
ISSN 0108-2701 ©1995