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Acta Cryst. (1996). **C52**, 2045–2047

2-Acetylphenyl 1-Naphthoate

ANDRÉS E. GOETA,^a GRACIELA PUNTE,^a JORGE L. JOS^b
AND JUAN C. AUTINO^b

^a*Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, CC67–(1900)–La Plata, Argentina, and* ^b*LADECOM-CONICET, Laboratorio de Estudio de Compuestos Orgánicos, Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Argentina. E-mail: goeta@ayelen.fisica.unlp.edu.ar*

(Received 3 January 1995; accepted 29 January 1996)

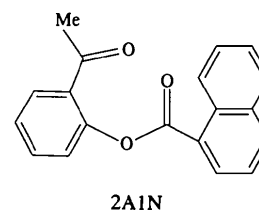
Abstract

The crystal structure of the title compound, C₁₉H₁₄O₃, an intermediate in the synthesis of 2-naphthylchromones, has been determined by X-ray diffraction. The title molecule, which can be viewed as the fusion of 1-naphthoic acid and acetophenone, is not planar. The dihedral angle between the benzene and naphthalene planes is 77.39 (7)°. Two intramolecular C—H···O bonds and a short intramolecular O···O distance of 2.719 (2) Å have been observed.

Comment

2-Acetylphenyl 1-naphthoate (2A1N) belongs to the family of 2-acetylphenyl naphthoates which are potentially important intermediates in the synthesis of several compounds with different kinds of activities, e.g. antimicrobial (Vibhute, 1976) and antitumor (Atassi, Briet, Berthelon & Collonges, 1985). 2A1N was synthesized by means of a known reaction (Virkar & Shah, 1942).

An exhaustive search of the Cambridge Structural Database (Allen & Kennard, 1993) showed that the only related compounds already solved are 1-naphthoic



acid (1NA) (Trotter, 1960) and acetophenone (AP) (Tanimoto, Kobayashi, Nagakura & Saito, 1973). The phenyl and naphthalene rings are essentially planar. The dihedral angle between the benzene mean plane (BMP) and the naphthalene mean plane (NMP) is 77.39 (7)°. The angle formed between the carboxyl mean plane and NMP is 14.3 (2)° in 2A1N (11° in 1NA), and the angle between the carboxyl group and BMP is 88.3 (2)°.

Comparison of the geometry of the bridging carboxyl group in 2A1N with that of the carboxyl group in 1NA displays a noticeable variation in bond lengths and angles. The C(9)—C(8)—O(1) and O(1)—C(8)—O(2) angles alter from 122 to 111.0 (1)° and from 110 to 121.7 (1)° in 2A1N and 1NA, respectively, and the bond length O(1)—C(8) stretches from 1.28 to 1.360 (2) Å. Although the structure of 1NA was determined from film data, we think that the differences are large enough to permit the assumption of a variation in the character of the C—O bond. There is also a significant change in the dihedral angle between the mean planes formed by O(3)—C(10)—C(21) and BMP from a value of 4.0 (2) in AP to 24.9 (2)° in 2A1N. These large modifications in the carboxyl and acetophenone group geometry may be a result of the short intramolecular contact between O(1) and O(3) [2.719 (2) Å] in 2A1N. There is some evidence of short intramolecular contacts between O atoms in the literature (Punte, Rivero, Cerdeira & Nudelman, 1990; Faerman *et al.*, 1985), but this has not been discussed thoroughly.

In addition to the short distance mentioned above, we have found two intramolecular D—H···A interactions. These are C(13)—H(131)···O(1) and C(15)—H(151)···O(2), where the C···O distances are 2.652 (2) and 2.886 (2) Å, the H···O distances are 2.28 (2) and

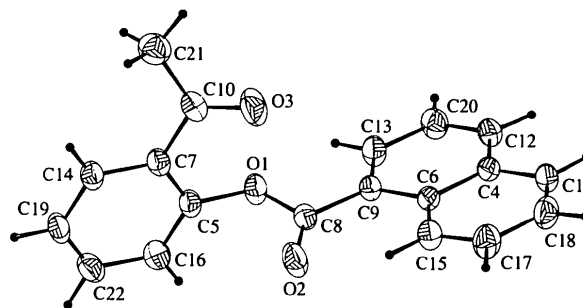


Fig. 1. The molecular structure of 2A1N showing 50% probability displacement ellipsoids for non-H atoms and H atoms as small spheres of arbitrary radii.

2.22 (2) Å, and the C—H...O angles are 102.3 (16) and 125.5 (15)°, respectively. The three interactions referred to here are far less than the sum of the van der Waals radii (Bondi, 1964) and the last two can be classified as hydrogen bonds according to Taylor & Kennard (1982). No significant intermolecular distances have been found.

Experimental

2A1N was synthesized by means of a known reaction (Virkar & Shah, 1942). The single crystal used for analysis was obtained by constant-volume crystallization of its methanolic solution saturated at 308 K, which was cooled slowly to 293 K and allowed to stand for 20 h.

Crystal data

C₁₉H₁₄O₃
M_r = 290.32
 Monoclinic
*P*2₁/*n*
a = 11.9292 (5) Å
b = 8.8839 (5) Å
c = 14.214 (1) Å
 β = 105.089 (4)°
V = 1454.4 (1) Å³
Z = 4
D_x = 1.33 Mg m⁻³

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 62 reflections
 θ = 9.823–24.881°
 μ = 0.083 mm⁻¹
T = 295 K
 Prism
 0.30 × 0.20 × 0.20 mm
 Colourless

Data collection

Siemens *P4* diffractometer
 2θ/ ω scans
 Absorption correction: none
 4451 measured reflections
 3037 independent reflections
 1972 observed reflections
 [*I* > 3.0σ(*I*)]
R_{int} = 0.007

θ_{\max} = 27.50°
h = -1 → 15
k = -1 → 11
l = -18 → 18
 3 standard reflections monitored every 97 reflections
 intensity decay: 2.23%

Refinement

Refinement on *F*
R = 0.034
wR = 0.041
S = 1.15
 1972 reflections
 255 parameters
 All H-atom parameters refined
 $w = w' [1 - \{\Delta F/6\sigma(F)\}^2]^2$

(Δ/σ)_{max} = 0.002
 $\Delta\rho_{\max}$ = 0.18 e Å⁻³
 $\Delta\rho_{\min}$ = -0.18 e Å⁻³
 Extinction correction: none
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol IV, Table 2.2B)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
O(1)	0.00913 (8)	0.6393 (1)	0.65656 (7)	0.0478 (3)
O(2)	-0.0587 (1)	0.4486 (2)	0.7280 (1)	0.0721 (4)
O(3)	-0.0344 (1)	0.7843 (2)	0.81176 (9)	0.0809 (5)
C(4)	0.2992 (1)	0.4021 (2)	0.9102 (1)	0.0416 (4)
C(5)	-0.1044 (1)	0.6852 (2)	0.6100 (1)	0.0422 (4)
C(6)	0.1781 (1)	0.4133 (2)	0.86211 (9)	0.0381 (4)

C(7)	-0.1591 (1)	0.7944 (2)	0.6528 (1)	0.0421 (4)
C(8)	0.0219 (1)	0.5240 (2)	0.7214 (1)	0.0430 (4)
C(9)	0.1459 (1)	0.5057 (2)	0.77624 (9)	0.0398 (4)
C(10)	-0.1055 (1)	0.8561 (2)	0.7525 (1)	0.0514 (5)
C(11)	0.3343 (1)	0.3123 (2)	0.9954 (1)	0.0519 (5)
C(12)	0.3813 (1)	0.4783 (2)	0.8725 (1)	0.0512 (5)
C(13)	0.2295 (1)	0.5795 (2)	0.7438 (1)	0.0501 (5)
C(14)	-0.2680 (1)	0.8445 (2)	0.5989 (1)	0.0482 (5)
C(15)	0.0992 (1)	0.3341 (2)	0.9030 (1)	0.0493 (5)
C(16)	-0.1541 (2)	0.6299 (2)	0.5179 (1)	0.0540 (5)
C(17)	0.1372 (2)	0.2500 (2)	0.9857 (1)	0.0604 (6)
C(18)	0.2563 (2)	0.2391 (2)	1.0326 (1)	0.0592 (6)
C(19)	-0.3196 (1)	0.7869 (2)	0.5079 (1)	0.0539 (5)
C(20)	0.3478 (1)	0.5657 (2)	0.7917 (1)	0.0566 (5)
C(21)	-0.1418 (2)	1.0086 (3)	0.7777 (2)	0.0677 (6)
C(22)	-0.2632 (2)	0.6804 (2)	0.4673 (1)	0.0588 (5)

Table 2. Selected geometric parameters (Å, °)

O(1)—C(5)	1.404 (2)	C(7)—C(14)	1.398 (2)
O(1)—C(8)	1.360 (2)	C(8)—C(9)	1.490 (2)
O(2)—C(8)	1.196 (2)	C(9)—C(13)	1.370 (2)
O(3)—C(10)	1.210 (2)	C(10)—C(21)	1.494 (3)
C(4)—C(6)	1.431 (2)	C(11)—C(18)	1.351 (3)
C(4)—C(11)	1.420 (2)	C(12)—C(20)	1.358 (2)
C(4)—C(12)	1.407 (2)	C(13)—C(20)	1.403 (2)
C(5)—C(7)	1.394 (2)	C(14)—C(19)	1.379 (2)
C(5)—C(16)	1.379 (2)	C(15)—C(17)	1.367 (2)
C(6)—C(9)	1.438 (2)	C(16)—C(22)	1.388 (2)
C(6)—C(15)	1.415 (2)	C(17)—C(18)	1.406 (3)
C(7)—C(10)	1.498 (2)	C(19)—C(22)	1.372 (3)
C(5)—O(1)—C(8)	117.6 (1)	C(6)—C(9)—C(13)	120.1 (1)
C(6)—C(4)—C(11)	118.9 (1)	C(8)—C(9)—C(13)	118.8 (1)
C(6)—C(4)—C(12)	120.1 (1)	O(3)—C(10)—C(7)	121.0 (2)
C(11)—C(4)—C(12)	121.0 (1)	O(3)—C(10)—C(21)	120.4 (2)
O(1)—C(5)—C(7)	120.0 (1)	C(7)—C(10)—C(21)	118.6 (2)
O(1)—C(5)—C(16)	117.9 (1)	C(4)—C(11)—C(18)	121.6 (1)
C(7)—C(5)—C(16)	121.8 (1)	C(4)—C(12)—C(20)	121.1 (1)
C(4)—C(6)—C(9)	117.3 (1)	C(9)—C(13)—C(20)	121.5 (1)
C(4)—C(6)—C(15)	117.8 (1)	C(7)—C(14)—C(19)	121.3 (2)
C(9)—C(6)—C(15)	124.9 (1)	C(6)—C(15)—C(17)	121.2 (1)
C(5)—C(7)—C(10)	122.3 (1)	C(5)—C(16)—C(22)	119.4 (2)
C(5)—C(7)—C(14)	117.1 (1)	C(15)—C(17)—C(18)	120.9 (2)
C(10)—C(7)—C(14)	120.6 (1)	C(11)—C(18)—C(17)	119.7 (2)
O(1)—C(8)—O(2)	121.7 (1)	C(14)—C(19)—C(22)	120.2 (1)
O(1)—C(8)—C(9)	111.0 (1)	C(12)—C(20)—C(13)	119.9 (2)
O(2)—C(8)—C(9)	127.3 (1)	C(16)—C(22)—C(19)	120.1 (2)
C(6)—C(9)—C(8)	121.1 (1)		

The structure was solved by direct methods and refined by full-matrix least squares.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *CRYSTALS* (Watkin, Carruthers & Betteridge, 1990). Molecular graphics: *CRYSTALS*. Software used to prepare material for publication: *CRYSTALS*, *PLATON* (Spek, 1990).

The authors would like to acknowledge Professor J. A. K. Howard for providing the experimental facilities and CONICET and UNLP for financial support. AEG would like to acknowledge CONICET, The British Council and Fundación Antorchas for a research fellowship. JLJ also thanks CICPBA for a research fellowship.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: CR1187). 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. (1996). **C52**, 2047–2049

1,3-Bis(2-methylphenyl)-2-(4-morpholino)-isothiourea

L. SUDHA,^a J. SENTHIL SELVAN,^a K. SUBRAMANIAN,^{a*} TH. STEINER,^b G. KOELLNER,^b N. SRINIVASAN^c AND K. RAMDAS^c

^aDepartment of Physics, Anna University, Madras 25, India,

^bInstitut für Kristallographie, Freie Universität Berlin, Takustraße 6, D-14195 Berlin, Germany, and ^cSPIC Science Foundation, Madras 25, India

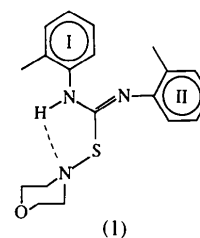
(Received 6 December 1995; accepted 16 February 1996)

Abstract

The title molecule, C₁₉H₂₃N₃OS, consists of two aromatic rings and a morpholine ring attached to an isothiourea moiety. The morpholine ring adopts a chair conformation and the sum of the angles around the N atom is 337.5 (2)°. The molecular conformation is stabilized by an intramolecular N—H···N hydrogen bond.

Comment

The molecular conformation and atomic numbering scheme of the title compound, (1), are shown in Fig. 1. We have previously reported the crystal structures of related compounds (Sudha, Senthil Selvan, Subramanian, Steiner, Koellner, Srinivasan & Ramdas, 1995*a,b*).



The morpholine ring in (1) is in a chair conformation. A survey of structures with morpholine rings shows wide variability of the N-atom pyramidality, with the sum of the angles at the N atom ranging from 336 to 359° (Wong-Ng, Nyburg, Awwal, Jankie & Kresge, 1982). In the present case, the sum of the angles at N(12) is 337.5 (2)°. The morpholine ring is oriented in such a way that the N(12) lone pair can accept an intramolecular hydrogen bond from the N(8)—H group [N···N 2.724 (3) and H···N 2.07 Å; Fig. 1 and Table 3]. To achieve this favourable intramolecular interaction, the torsion angle N(8)—C(9)—S(11)—N(12) has a value of −1.0 (2)°, while the best planes of the isothiourea and morpholino groups are almost perpendicular to one another [dihedral angle 88.6 (1)°]. The geometry around the S atom is normal [N—S 1.708 (2), C—S 1.801 (3) Å and N—S—C 101.2 (1)°].

The two aromatic rings have very different orientations. Ring II is almost perpendicular to the isothiourea moiety [angle between least-squares planes 85.2 (1)°], thereby avoiding short intramolecular contacts. This is the geometry that we have typically observed in related compounds (Sudha *et al.*, 1995*a,b*). Ring I, however, is located almost in the isothiourea plane [angle between least-squares planes 15.9 (2)°; torsion angles C(2)—C(1)—N(8)—C(9) 171.1 (2) and C(1)—N(8)—C(9)—N(10) −7.5 (4)°]. This leads to an unusually short intramolecular C(6)—H···N(10) contact, with H···N

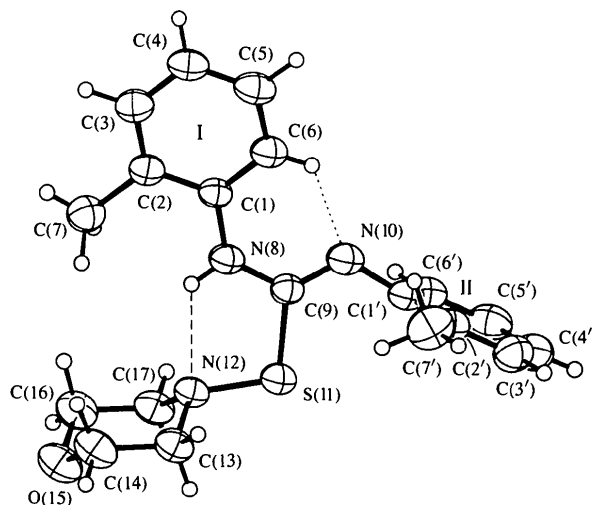


Fig. 1. The molecular structure and atomic numbering scheme of (1). Displacement ellipsoids are shown at the 30% probability level.