

Fig. 2. Some Newman projections (angles in °).

The sugar chain C(10)—C(11)—C(12)—C(13)—C(14) is planar [maximum deviation 0.014 (11) Å]. The orientation of the acetoxy groups with respect to the sugar chain is defined by the torsion angles: C(13)—C(14)—O(14)—C(114) = 144.5 (10), C(14)—C(13)—O(13)—C(113) = -113.0 (11), C(13)—C(12)—O(12)—C(112) = 106.0 (11), C(12)—C(11)—O(11)—C(111) = 130.7 (11) and C(11)—C(10)—O(10)—C(110) = 135.0 (10)°. Bond lengths are in good agreement with those in analogous compounds.

Fig. 2 shows the Newman projections corresponding to the C—C bonds of the sugar chain. The configurations around the chiral centres C(13), C(12), C(11) and C(10) are *R*, *S*, *R* and *S*, respectively (Klyne & Prelog, 1960), in accordance with the *D*-galacto constitution.

The dihedral angle between the pyrazole and phenyl rings is 25.9 (4)°, and that between the pyrazole ring and the *galacto* chains is 57.5 (7)°.

The intermolecular linkages are due to van der Waals forces and there are no abnormal intermolecular distances.

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1-Ethynyl-2,7-dimethoxynaphthalene: an Example of Hydrogen Bonding Between an Ethynylic Hydrogen and a Methoxyl Oxygen

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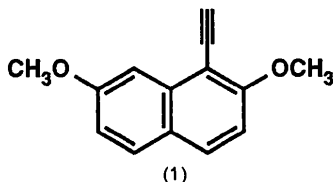
Abstract. C₁₄H₁₂O₂, *M_r* = 212.3, triclinic, *P* $\bar{1}$, *a* = 6.6160 (12), *b* = 11.359 (2), *c* = 16.217 (2) Å, α = 80.640 (11), β = 86.305 (13), γ = 78.858 (12)°, *V* = 1179.2 (4) Å³, *Z* = 4, *D_x* = 1.196 g cm⁻³, λ (Cu *K* α) = 1.54184 Å, μ = 6.01 cm⁻¹, *F*(000) = 448, *T* = 295 K, *R* = 0.039 for 3488 observations (of 4844 unique data). The crystal consists of two independent molecules related by a C—H...O contact. The donor is the ethynylic H on one molecule, and the acceptor

is the methoxyl O *ortho* to the ethynylic group on the other molecule. The $\equiv\text{C—H}\cdots\text{O}$ bond length (C to O distance) is 3.260 (2) Å and the angle at H is 164 (1)°. The naphthalene ring system of the two independent molecules shows an average deviation from planarity of 0.007 (2) and 0.008 (2) Å with respective maximum deviations of 0.015 (1) and 0.014 (2) Å.

Introduction. The title compound, (1), prepared by the reaction of 1-acetyl-2,7-dimethoxynaphthalene

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and diethyl chlorophosphate with lithium diisopropylamide in tetrahydrofuran at 195 K (Negishi, King & Klima, 1980), is a building block in the preparation of dinaphthylethyne. These latter compounds will be used as models in the study of molecular recognition. The title compound recognizes itself in the crystal by forming an intermolecular hydrogen bond between two independent molecules in the unit cell. Hydrogen bonds between ethynylic hydrogen and ethereal oxygen are rare and worthy of discussion.



Experimental. Sublimation produced colorless needles of (1), m.p. 373–374 K. Crystal size 0.20 × 0.25 × 0.38 mm, capillary mounted in random orientation on an Enraf–Nonius CAD-4 computer-controlled κ -axis diffractometer equipped with a graphite monochromator, $\lambda(\text{Cu } K\alpha) = 1.54184 \text{ \AA}$. Cell dimensions from setting angles of 25 reflections having $25 < \theta < 30^\circ$. Successful refinement of a centrosymmetric model determined the space group as $P\bar{1}$.

Data having $2 < 2\theta < 75^\circ$, $0 \leq h \leq 8$, $-14 \leq k \leq 14$, $-20 \leq l \leq 20$ were collected using ω - 2θ scans designed for $I = 25\sigma(I)$, subject to max. scan time of 120 s, scan rates varied 0.61 – $3.30^\circ \text{ min}^{-1}$. No redundant data were measured. Three reflections (200, 040, 003), measured every 10 000 s, showed a small intensity loss; thus a linear decay correction was applied, with correction factors ranging from 1.000 to 1.0211. Lorentz and polarization corrections were applied. ψ scans showed no intensity variation with rotation about the scattering vector, so no absorption correction was applied. The extinction coefficient was refined in the least squares to $g = 4.2(2) \times 10^{-6}$, where the correction factor $(1 + gI_c)^{-1}$ was applied to F_c .

Structure solved by direct methods, using *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982), and successive difference Fourier syntheses. The structure was refined by weighted full-matrix least squares; non-H atoms refined anisotropically, and H atoms refined isotropically.

The function minimized was $\sum w(|F_o| - |F_c|)^2$ and weights were assigned as $w = 4F_o^2 \text{Lp}[S^2(C + R^2B) + (0.02F_o^2)^2]^{-1}$, where S = scan rate, C = total integrated peak count, R = scan time/background counting time, B = total background count, Lp = Lorentz-polarization factor, using Enraf–Nonius

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
O1A	0.6016 (2)	0.40733 (9)	0.61272 (6)	6.20 (3)
O2A	-0.0454 (2)	0.03932 (9)	0.87157 (6)	5.85 (2)
C1A	0.5496 (2)	0.3537 (1)	0.69054 (9)	4.77 (3)
C2A	0.6400 (2)	0.3672 (1)	0.76371 (9)	5.41 (3)
C3A	0.5752 (2)	0.3128 (1)	0.83925 (9)	5.45 (3)
C4A	0.4189 (2)	0.2433 (1)	0.84691 (8)	4.65 (3)
C5A	0.3501 (3)	0.1858 (1)	0.92500 (8)	5.55 (4)
C6A	0.2002 (3)	0.1194 (1)	0.93062 (8)	5.54 (4)
C7A	0.1062 (2)	0.1071 (1)	0.85734 (8)	4.63 (3)
C8A	0.1689 (2)	0.1592 (1)	0.78039 (8)	4.27 (3)
C9A	0.3268 (2)	0.2284 (1)	0.77323 (8)	4.04 (3)
C10A	0.3974 (2)	0.2846 (1)	0.69417 (8)	4.19 (3)
C11A	0.3104 (2)	0.2682 (1)	0.61912 (8)	4.60 (3)
C12A	0.2386 (3)	0.2490 (2)	0.55930 (9)	5.99 (4)
C13A	0.7571 (3)	0.4810 (2)	0.6042 (1)	7.56 (5)
C14A	-0.1419 (2)	0.0173 (1)	0.8009 (1)	6.19 (4)
O1B	-0.0525 (2)	0.1811 (1)	0.42599 (6)	7.55 (3)
O2B	0.5959 (2)	0.32917 (9)	0.06326 (6)	6.06 (3)
C1B	-0.0295 (2)	0.2555 (1)	0.35218 (9)	5.77 (4)
C2B	-0.1802 (3)	0.3536 (2)	0.3189 (1)	7.26 (4)
C3B	-0.1433 (3)	0.4215 (2)	0.2444 (1)	6.82 (4)
C4B	0.0429 (2)	0.3974 (1)	0.19873 (9)	5.28 (3)
C5B	0.0836 (3)	0.4659 (1)	0.1203 (1)	6.08 (4)
C6B	0.2632 (3)	0.4408 (1)	0.07797 (9)	5.79 (4)
C7B	0.4196 (2)	0.3442 (1)	0.11157 (8)	4.83 (3)
C8B	0.3877 (2)	0.2750 (1)	0.18675 (8)	4.34 (3)
C9B	0.1984 (2)	0.2994 (1)	0.23223 (8)	4.31 (3)
C10B	0.1584 (2)	0.2284 (1)	0.31011 (8)	4.64 (3)
C11B	0.3113 (2)	0.1277 (1)	0.34351 (8)	5.23 (3)
C12B	0.4386 (3)	0.0441 (2)	0.3678 (1)	7.38 (5)
C13B	-0.2437 (3)	0.2045 (2)	0.4739 (1)	10.69 (7)
C14B	0.7544 (3)	0.2281 (2)	0.0895 (1)	6.57 (4)

SDP (Frenz, 1980), scattering factors of Cromer & Waber (1974), anomalous coefficients of Cromer (1974). Of 4844 unique data, 3488 reflections with $I > 3\sigma(I)$ were used in the refinement. The final cycle included 386 variables and converged (largest $\Delta/\sigma = 0.11$) to $R = 0.039$, $wR = 0.051$, $R(\text{all}) = 0.059$, and $S = 2.223$.

Discussion. Table 1 presents the final coordinates* and equivalent isotropic thermal parameters, and Table 2 presents bond distances and angles. Fig. 1 illustrates the molecules and the numbering scheme, and Fig. 2 shows the unit cell.

Two independent molecules form the asymmetric unit. The ethynylic hydrogen of molecule *A* hydrogen bonds to the methoxy *ortho* to the ethynyl group in molecule *B*. The ethynylic hydrogen of molecule *B* does not hydrogen bond. Within three standard deviations, bond lengths are identical for both molecules (see Table 2), except for O1–C13 and

* Tables of H-atom coordinates, bond distances and angles involving H atoms, anisotropic thermal parameters, least-squares planes and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52888 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

O1A—C1A	1.363 (2)	O1B—C1B	1.366 (2)
O1A—C13A	1.433 (2)	O1B—C13B	1.444 (2)
O2A—C7A	1.365 (2)	O2B—C7B	1.361 (2)
O2A—C14A	1.426 (2)	O2B—C14B	1.425 (2)
C1A—C2A	1.405 (2)	C1B—C2B	1.404 (2)
C1A—C10A	1.384 (2)	C1B—C10B	1.385 (2)
C2A—C3A	1.362 (2)	C2B—C3B	1.359 (2)
C3A—C4A	1.405 (2)	C3B—C4B	1.399 (2)
C4A—C5A	1.417 (2)	C4B—C5B	1.418 (2)
C4A—C9A	1.424 (2)	C4B—C9B	1.423 (2)
C5A—C6A	1.348 (2)	C5B—C6B	1.338 (2)
C6A—C7A	1.415 (2)	C6B—C7B	1.418 (2)
C7A—C8A	1.366 (2)	C7B—C8B	1.367 (2)
C8A—C9A	1.413 (2)	C8B—C9B	1.415 (2)
C9A—C10A	1.429 (2)	C9B—C10B	1.423 (2)
C10A—C11A	1.433 (2)	C10B—C11B	1.430 (2)
C11A—C12A	1.176 (2)	C11B—C12B	1.174 (2)

C1A—O1A—C13A	118.9 (1)	C1B—O1B—C13B	118.3 (1)
C7A—O2A—C14A	117.9 (1)	C7B—O2B—C14B	117.8 (1)
O1A—C1A—C2A	123.4 (1)	O1B—C1B—C2B	124.5 (1)
O1A—C1A—C10A	115.8 (1)	O1B—C1B—C10B	115.1 (1)
C2A—C1A—C10A	120.9 (1)	C2B—C1B—C10B	120.4 (1)
C1A—C2A—C3A	119.6 (1)	C1B—C2B—C3B	120.0 (1)
C2A—C3A—C4A	122.1 (1)	C2B—C3B—C4B	122.0 (1)
C3A—C4A—C5A	122.8 (1)	C3B—C4B—C5B	123.0 (1)
C3A—C4A—C9A	118.9 (1)	C3B—C4B—C9B	118.6 (1)
C5A—C4A—C9A	118.3 (1)	C5B—C4B—C9B	118.4 (1)
C4A—C5A—C6A	121.7 (1)	C4B—C5B—C6B	121.7 (1)
C5A—C6A—C7A	119.8 (1)	C5B—C6B—C7B	120.1 (1)
O2A—C7A—C6A	114.1 (1)	O2B—C7B—C6B	114.5 (1)
O2A—C7A—C8A	125.0 (1)	O2B—C7B—C8B	125.0 (1)
C6A—C7A—C8A	120.9 (1)	C6B—C7B—C8B	120.5 (1)
C7A—C8A—C9A	120.1 (1)	C7B—C8B—C9B	120.3 (1)
C4A—C8A—C9A	119.3 (1)	C4B—C8B—C9B	119.0 (1)
C4A—C9A—C10A	118.6 (1)	C4B—C9B—C10B	119.0 (1)
C8A—C9A—C10A	122.1 (1)	C8B—C9B—C10B	121.9 (1)
C1A—C10A—C9A	120.0 (1)	C1B—C10B—C9B	119.9 (1)
C1A—C10A—C11A	120.5 (1)	C1B—C10B—C11B	120.4 (1)
C9A—C10A—C11A	119.5 (1)	C9B—C10B—C11B	119.7 (1)
C10A—C11A—C12A	176.7 (1)	C10B—C11B—C12B	177.4 (2)

C5—C6, which differ by 0.011 and 0.010 Å, respectively. Differences in bond angles are less than 0.7°, except for O1—C1—C2, which differs by 1.1°. The ethynylic bonds are not precisely linear [angles of 176.7 (1) and 177.4 (2)°], a result seen in 1,4-diethynylbenzene (Ahmed, Kitaigorodsky & Sirota, 1972) (angles of 178.6°) and 1,4-diethynyl-naphthalene (Enkelmann & Rohde, 1977) [angles from 175.8 (10) to 177.5 (10)°].

The H12A...O1B distance [2.37 (2) Å] is notably less than the sum of the van der Waals radii, 2.6 Å, for hydrogen and oxygen (Pauling, 1960). The C12A—H12A—O1B angle of 164 (1)° satisfies the geometric criterion for hydrogen bonding in short C—H...O contacts (Taylor & Kennard, 1982). The C1B—O1B—H12A (or C12A) angle of 103 (1) [or 106.8 (1)°] and C10B—C1B—O1B—H12A (or C12A) torsion angle of 69 (1) [or 72.2 (2)°] suggests interaction with a hybridized lone-pair orbital of the oxygen.

Comparison of (1) with previous structures involving an ethynylic hydrogen bond to oxygen (Ferguson & Islam, 1966; Calabrese, McPhail & Sim, 1966; Ferguson & Tyrrell, 1965; Leiserowitz & Tuval,

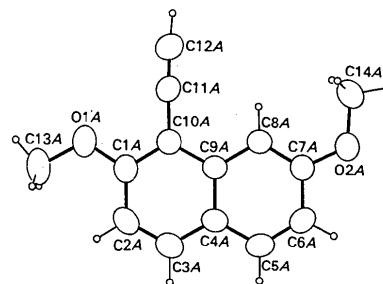


Fig. 1. Numbering scheme and thermal ellipsoids drawn at the 40% probability level for molecule A. H atoms are drawn as circles with the same arbitrary radius.

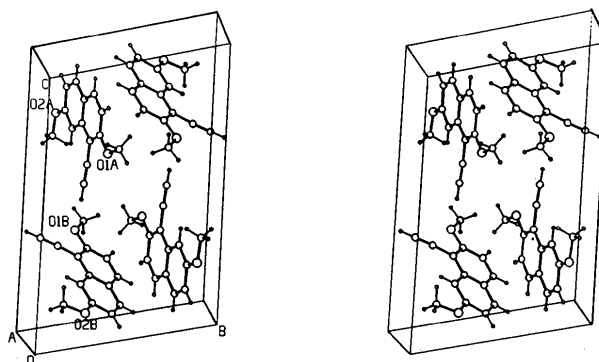


Fig. 2. Stereoview of the unit cell.

Table 3. Distances (Å) and angles (°) of ethynylic hydrogen-to-oxygen hydrogen bonds

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
H...O	2.37 (2)	2.19	2.39	—	2.2	—	—
C...O	3.260 (2)	3.21	3.45	3.26	3.293 (3)	3.29, 3.22	—
C—H...O	164.3 (14)	161.9	156	—	120	167 (3)	—
C≡C	1.176 (2)	1.195 (9)	1.18 (2)	—	1.164 (2)	1.179 (3)	1.21

References: (1) this work; (2) *o*-chlorobenzoylacetylene (Ferguson & Islam, 1966); (3) propargyl 2-bromo-3-nitrobenzoate (Calabrese, McPhail & Sim, 1966); (4) *o*-bromobenzoylacetylene (Ferguson & Tyrrell, 1965); (5) *N*-methylpropiolamide (Leiserowitz & Tuval, 1978); (6) 1-chloro-3-ethynyl-2,4-dimethoxybenzene (Evans, Fronczek & Gandour, 1989); (7) lauricin (Cameron, Cheung, Ferguson & Robertson, 1969).

1978; Evans, Fronczek & Gandour, 1989; Cameron, Cheung, Ferguson & Robertson, 1969) shows that the bond distances and angles involving the hydrogen bonds are very similar (Table 3). In (2), (3), (4) and (5) carbonyl oxygens accept the hydrogen bond; in (6), the acceptor is a methoxyl oxygen; but in (7), the hydrogen bond forms a bifurcated structure with an ether and an ester. The comparable strength of these weak hydrogen bonds is shown by the similar values of C...O distances, except for compound (3) in which the interaction seems to be much weaker. The ≡C—H...O angles are typical of more polar hydrogen bonds (Murray-Rust & Glusker, 1984), but the distances are considerably longer. Although weak, these interactions determine molecular packing and

conformation (Berkovitch-Yellin & Leiserowitz, 1984).

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Structure of *N*-Methylnicotinamide

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Abstract. $C_7H_8N_2O$, $M_r = 136.2$, monoclinic, $P2_1/a$, $a = 7.055$ (1), $b = 9.849$ (6), $c = 10.066$ (4) Å, $\beta = 100.47$ (2)°, $V = 687.5$ (5) Å³, $Z = 4$, $D_m = 1.32$, $D_x = 1.315$ g cm⁻³, $Cu K\alpha$, $\lambda = 1.5418$ Å, $\mu = 7.09$ cm⁻¹, $F(000) = 288$, $T = 294$ K, $R = 0.048$ for 1134 reflections [$I > 3\sigma(I)$]. The *N*-methylcarboxamide group is extended with the keto O(7) *transoid* to C(2) [C(2)—C(3)—C(7)—O(7) ± 158.9 (3), C(3)—C(7)—N(7)—C(8) ± 177.1 (3), C(2)—C(3)—C(7)—N(7) ± 23.2 (3) and C(4)—C(3)—C(7)—N(7) ± 158.2 (3)°]. The dihedral angle between the planes of the pyridine ring and the carboxamide plane is 22°. The molecules are linked together by N—H···O hydrogen bonds involving the amino N(7) and the carbonyl O(7) atoms.

Introduction. Nicotinamide is a component of two related coenzymes, nicotinamide adenine dinucleotide (NAD) and nicotinamide adenine dinucleotide diphosphate (NADP). The crystal structure of NAD has been determined in both the free acid form (Parthasarathy & Fridey, 1984) and in the low pH

lithium salt (Reddy, Saenger, Muhlegger & Weimann, 1981). Although they had different conformations for the NAD molecules, both the structures revealed intermolecular stacking of the bases; however, no intramolecular stacking was observed as predicted by NMR studies (Sarma, Ross & Kaplan, 1968). We have undertaken a systematic analysis of several model compounds involving the bases and nicotinamide groups, with a view to studying the stacking properties in these compounds and comparing them with those found in NAD. The crystal structure of adenosine 5'-mononicotinate (Ramasubbu & Parthasarathy, 1988) revealed intra- as well as intermolecular base stacking, a feature not observed in some other model compounds studied earlier (Sakaki, Inoue, Senda & Tomita, 1978; Voet, 1973; Johnson, Frank & Paul, 1973). Recently, we determined the crystal structures of thionicotinamide and *N*-methylnicotinamide with a view to obtaining accurate molecular dimensions of neutral nicotinamide as well as studying the effect of sulfur substitution on its hydrogen-bonding details. We report here the crystal structure of *N*-methylnicotinamide.

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