Methyl 8-[(2,7-Dimethoxynaphthyl)ethynyl]-7-methoxy-2-naphthoate

By Philippe Prince, Frank R. Fronczek and Richard D. Gandour*

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, USA

Abstract. $C_{27}H_{22}O_5$, $M_r = 426.5$, monoclinic, $P2_1/c$, $a = 13.703 (2)$, $b = 9.122 (2)$, $c = 18.028 (2)$ Å, $\beta = 107.15 (1)°$, $V = 2153.2 (11)$ Å^3, $Z = 4$, $D_x = 1.316$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1.54184$ Å, $\mu = 6.97$ cm^{-1}, $F(000) = 896$, $T = 301$ K, $R = 0.063$ for 3615 observations (of 4433 unique data). The average deviations from planarity are 0.008 (2) Å with a maximum of 0.018 (2) Å for the dimethoxynaphthyl ring, and 0.006 (2) Å with a maximum of 0.010 (2) Å for the naphthoate ring. The dihedral angle between the two rings is 3.8 (4)°. The two methoxy groups on the dimethoxynaphthyl ring are nearly coplanar with the ring, with C—C—O—C torsion angles of 3.1 (2)° for that *ortho* to the triple bond, and 3.5 (2)° for the other. The methoxy group on the naphthoate ring is also nearly coplanar with the ring, with a C—C—O—C torsion angle of −6.2 (2)°. The triple-bond distance is 1.191 (2) Å, and bond angles at the two ethynylic C atoms are 178.1 (1) and 177.5 (1)°. The molecule adopts an *anti* conformation about the C—C≡C—C axis.

Experimental. The title compound (1), was prepared by the palladium-catalyzed coupling (Carson, Almond, Brannan, Carmosin, Flaim, Gill, Gleason, Keely, Ludovici, Pitis, Rebarchak & Villani, 1988) of 2,7-dimethoxy-1-ethynylnaphthalene and methyl 8-iodo-7-methoxy-2-naphthoate in diethylamine.
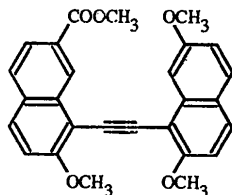
Yellow crystals of (1), m.p. 518–519 K, were isolated by slow evaporation of acetone. A fragment of size $0.15 \times 0.28 \times 0.48$ mm, mounted on a glass fiber in random orientation, was used for data collection on an Enraf–Nonius CAD-4 diffractometer equipped with Cu $K\alpha$ radiation and a graphite monochromator. Cell dimensions from setting angles of 25

Table 1. *Coordinates and equivalent isotropic thermal parameters*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
O1	0.52269 (8)	0.4100 (1)	0.30622 (6)	5.18 (2)
O2	0.43478 (7)	0.8555 (1)	0.52877 (6)	4.50 (2)
O3	0.09136 (8)	0.4407 (2)	0.12194 (7)	6.12 (3)
O4	0.25918 (9)	0.4131 (2)	0.16920 (7)	6.34 (3)
O5	0.80670 (9)	0.7541 (2)	0.66749 (6)	5.64 (3)
C1	0.70460 (9)	0.5541 (2)	0.48183 (7)	3.47 (3)
C2	0.7960 (1)	0.4823 (2)	0.47972 (8)	3.98 (3)
C3	0.7932 (1)	0.3885 (2)	0.41758 (9)	4.79 (3)
C4	0.7056 (1)	0.3627 (2)	0.35936 (9)	4.91 (3)
C5	0.6141 (1)	0.4312 (2)	0.36089 (8)	4.10 (3)
C6	0.61311 (9)	0.5270 (2)	0.42047 (7)	3.48 (3)
C7	0.5198 (1)	0.5972 (2)	0.41982 (7)	3.34 (2)
C8	0.44327 (9)	0.6596 (2)	0.41917 (7)	3.28 (2)
C9	0.35032 (9)	0.7332 (1)	0.41487 (7)	3.25 (2)
C10	0.3464 (1)	0.8347 (2)	0.47134 (8)	3.65 (3)
C11	0.2547 (1)	0.9090 (2)	0.46704 (9)	4.38 (3)
C12	0.1692 (1)	0.8820 (2)	0.40749 (9)	4.52 (3)
C13	0.1684 (1)	0.7801 (2)	0.34843 (8)	3.94 (3)
C14	0.0799 (1)	0.7487 (2)	0.28625 (9)	4.68 (3)
C15	0.0820 (1)	0.6498 (2)	0.23037 (9)	4.57 (3)
C16	0.1738 (1)	0.5763 (2)	0.23286 (8)	3.82 (3)
C17	0.26082 (9)	0.6034 (2)	0.29289 (7)	3.45 (3)
C18	0.26056 (9)	0.7047 (2)	0.35196 (7)	3.34 (2)
C19	0.1810 (1)	0.4690 (2)	0.17270 (9)	4.41 (3)
C20	0.7064 (1)	0.6480 (2)	0.54446 (8)	3.77 (3)
C21	0.7958 (1)	0.6690 (2)	0.60291 (8)	4.28 (3)
C22	0.8863 (1)	0.5986 (2)	0.60099 (9)	4.72 (2)
C23	0.8862 (1)	0.5086 (2)	0.5418 (1)	4.66 (3)
C24	0.5176 (1)	0.3076 (2)	0.24587 (9)	5.23 (4)
C25	0.4383 (1)	0.9686 (2)	0.58401 (9)	5.22 (4)
C26	0.0920 (2)	0.3293 (3)	0.0639 (1)	8.01 (6)
C27	0.7167 (2)	0.8197 (2)	0.6765 (1)	5.97 (4)

---

reflections having $19 < \theta < 27°$. Space group determined to be $P2_1/c$ from systematic absences $h0l$ with l odd, $0k0$ with k odd.

A quadrant of data having $4 < 2\theta < 150°$, $0 \le h \le 17$, $0 \le k \le 11$, $-22 \le l \le 22$ was collected using ω–2θ scans designed for $I = 50\sigma(I)$, subject to maximum scan time $= 180$ s, scan rates varied 0.30–3.30° min^{-1}. Three reflections (200, 020, 002) were measured every 166 min, and their intensities exhibited only random fluctuations during data collection. A total of 5097 measurements were made. Lorentz and polarization corrections were applied. An empirical absorption correction based on a series of ψ scans was applied to the data. Relative transmission coefficients ranged from 0.8823 to 0.9975 with an average value of 0.9357. $R_{int} = 0.012$ for

---

* To whom correspondence should be addressed.

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

O1	C5	1.360 (2)	C7	C8	1.191 (2)
O1	C24	1.420 (2)	C8	C9	1.421 (2)
O2	C10	1.354 (1)	C9	C10	1.388 (2)
O2	C25	1.425 (2)	C9	C18	1.430 (2)
O3	C19	1.322 (2)	C10	C11	1.409 (2)
O3	C26	1.460 (3)	C11	C12	1.358 (2)
O4	C19	1.205 (2)	C12	C13	1.411 (2)
O5	C21	1.370 (2)	C13	C14	1.417 (2)
O5	C27	1.422 (3)	C13	C18	1.423 (2)
C1	C2	1.423 (2)	C14	C15	1.359 (2)
C1	C6	1.428 (2)	C15	C16	1.414 (2)
C1	C20	1.412 (2)	C16	C17	1.376 (2)
C2	C3	1.401 (2)	C16	C19	1.485 (2)
C2	C23	1.422 (2)	C17	C18	1.410 (2)
C3	C4	1.362 (2)	C20	C21	1.373 (2)
C4	C5	1.408 (2)	C21	C22	1.406 (2)
C5	C6	1.388 (2)	C22	C23	1.347 (2)
C6	C7	1.426 (2)			

C5	O1	C24	118.4 (1)	C10	C9	C18	119.5 (1)
C10	O2	C25	118.3 (1)	O2	C10	C9	115.8 (1)
C19	O3	C26	115.6 (1)	O2	C10	C11	123.8 (1)
C21	O5	C27	117.0 (1)	C9	C10	C11	120.4 (1)
C2	C1	C6	118.6 (1)	C10	C11	C12	120.2 (1)
C2	C1	C20	119.5 (1)	C11	C12	C13	122.0 (1)
C6	C1	C20	121.9 (1)	C12	C13	C14	123.0 (1)
C1	C2	C3	119.1 (1)	C12	C13	C18	118.4 (1)
C1	C2	C23	118.0 (1)	C14	C13	C18	118.6 (1)
C3	C2	C23	123.0 (1)	C13	C14	C15	121.3 (1)
C2	C3	C4	122.1 (1)	C14	C15	C16	120.3 (1)
C3	C4	C5	119.7 (2)	C15	C16	C17	119.7 (1)
O1	C5	C4	123.9 (1)	C15	C16	C19	122.6 (1)
O1	C5	C6	115.7 (1)	C17	C16	C19	117.7 (1)
C4	C5	C6	120.4 (1)	C16	C17	C18	121.1 (1)
C1	C6	C5	120.1 (1)	C9	C18	C13	119.5 (1)
C1	C6	C7	120.6 (1)	C9	C18	C17	121.7 (1)
C5	C6	C7	119.3 (1)	C13	C18	C17	118.9 (1)
C6	C7	C8	178.1 (1)	O3	C19	O4	122.7 (2)
C7	C8	C9	177.5 (1)	O3	C19	C16	112.7 (1)
C8	C9	C10	120.2 (1)	O4	C19	C16	124.6 (1)
C8	C9	C18	120.3 (1)	C1	C20	C21	120.0 (1)
O5	C21	C20	125.5 (1)	C21	C22	C23	120.2 (1)
O5	C21	C22	113.8 (1)	C2	C23	C22	121.6 (1)
C20	C21	C22	120.7 (1)				

averaging the redundant $0kl$ and $0k\bar{l}$ data. Structure solved by direct methods, using *SHELXS* (Sheldrick, 1985), and refined by full-matrix least squares. Non-hydrogen atoms refined anisotropically; H atoms were located from difference maps and refined isotropically except for those of the methyl group of the ester, which were placed in idealized positions with C—H 0.95 Å and $B = 1.3B_{eq}$ for C26.

The function minimized was $\sum w(|F_o| - |F_c|)^2$ and weights were assigned as $w = 4F_o^2 Lp[S^2(C + R^2B) + (0.02F_o^2)^2]^{-1}$, 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 *SDP* (Frenz & Okaya, 1980), scattering factors of Cromer & Waber (1974), anomalous coefficients of Cromer (1974). Of 4433 unique data, 3615 reflections having $I > 3\sigma(I)$ were used in the refinement. The extinction coefficient (Larson, 1969) was refined in the least squares to $g = 1.1$ (2) × 10^{-6}, where the correction factor $(1 + gI_c)^{-1}$ was applied to F_c; maximum correction 15.2% for the $12\bar{3}$ reflection. The

final cycle included 366 variables and converged (largest $\Delta/\sigma = 0.01$) with $R = 0.063$, $wR = 0.138$, $R(\text{all}) = 0.064$, and $S = 3.991$. The max. residual density was 0.33, min. -0.07 e Å^{-3}. Table 1 presents the final coordinates* and equivalent isotropic thermal parameters; Table 2 presents bond distances and angles. Fig. 1 illustrates the molecule and the numbering scheme; Fig. 2 shows the unit cell.

Related literature. Crystal structures of the uncoupled fragments: for 1-ethynyl-2,7-dimethoxy-naphthalene see Prince, Fronczek & Gandour (1990), for methyl 7-methoxy-2-naphthoate see Prince, Fronczek & Gandour (1991). For crystal structures
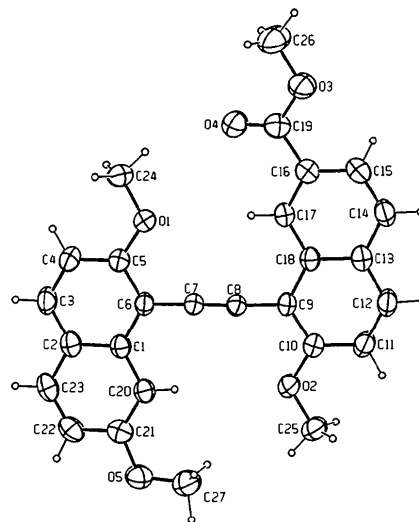
Fig. 1. Numbering scheme and thermal ellipsoids drawn at the 40% probability level. H atoms are drawn as circles with arbitrary radius.
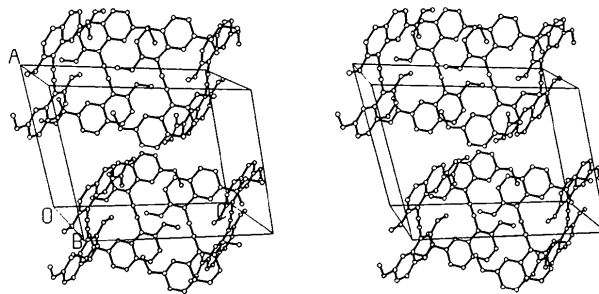

Fig. 2. Stereoview of the unit cell, viewed approximately down the b axis, with c horizontal.

of aromatic rings bridged by an ethynyl spacer see Prince, Evans, Fronczek & Gandour (1992), and references therein.

Support for this work is provided by grant CHE 8923033 from the National Science Foundation.

References

CARSON, J. R., ALMOND, H. R., BRANNAN, M. D., CARMOSIN, R. J., FLAIM, S. F., GILL, A., GLEASON, M. M., KEELY, S. L., LUDOVICI, D. W., PITIS, P. M., REBARCHAK, M. C. & VILLANI, F. J. (1988). *J. Med. Chem.* **31**, 630–636.

CROMER, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

FRENZ, B. A. & OKAYA, Y. (1980). *Enraf–Nonius Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.

LARSON, A. C. (1969). In *Crystallographic Computing*, edited by F. R. AHMED, S. R. HALL & C. P. HUBER, pp. 291–294. Copenhagen: Munksgaard.

PRINCE, P., FRONCZEK, F. R. & GANDOUR, R. D. (1990). *Acta Cryst.* C46, 1720–1723.

PRINCE, P., FRONCZEK, F. R. & GANDOUR, R. D. (1991). *Acta Cryst.* C47, 2226–2227.

PRINCE, P., EVANS, K. L., FRONCZEK, F. R. & GANDOUR, R. D. (1992). *Acta Cryst.* C48, 936–938.

SHELDRICK, G. M. (1985). In *Crystallographic Computing* 3, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD, pp. 175–179. Oxford Univ. Press.

Structure of the 3-Amino-1,2,4-triazolium Salt of 3-Nitro-1,2,4-triazol-5-one

BY LI JIA-RONG, CHEN BO-REN, OU YU-XIANG, CUI XIU-SHAN AND LIU ZUO-CAI

Department of Chemical Engineering, Beijing Institute of Technology, PO Box 327, Beijing 100081, People's Republic of China

Abstract. $C_2H_5N_4^+ \cdot C_2HN_4O_3^-$, $M_r = 214.2$, monoclinic, $P2_1/c$, $a = 6.539\,(2)$, $b = 19.063\,(8)$, $c = 6.749\,(4)$ Å, $\beta = 94.31\,(4)°$, $V = 838.9\,(6)$ Å^3, $Z = 4$, $D_m = 1.716$, $D_x = 1.700$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7069 Å, $\mu = 1.6$ cm^{-1}, $F(000) = 440$, room temperature, final $R = 0.047$ for 1679 unique observed reflections. The amine groups are planar with the five-membered ring of 1,2,4-triazole, the dihedral angles between cations and anions are 172.9° and the nitro groups are rotated 4.2° out of the plane of the triazolone. The proton is linked not at the amine group but at the 4-position of 3-amino-1,2,4-triazole, and the charge of the anions is mainly concentrated at the N_4 atom of 3-nitro-1,2,4-triazol-5-one. All H atoms except those on the C atom are involved in hydrogen bonds.

Experimental. The title compound (3ATNTO) was prepared by adding 3-amino-1,2,4-triazole to 3-nitro-1,2,4-triazol-5-one (NTO) dissolved in water. Yellow needle crystals for X-ray diffraction were crystallized from water solution. Dimensions 0.4 × 0.2 × 0.2 mm, automated Nicolet *R3m* diffractometer, Mo $K\alpha$ radiation monochromated by a graphite crystal, room temperature, θ–2θ scan, scan range $[2\theta(\alpha_1) - 1°] - [2\theta(\alpha_2) + 1°]$, variable scan speed, 7–29° min^{-1}.

20 centered reflections ($12 < 2\theta < 27°$) used for determining lattice parameters. No absorption corrections. Max. $(\sin\theta)/\lambda = 0.60$ Å^{-1}. Index range $0 < h < 8$, $0 < k < 23$, $-9 < l < 9$. 1679 reflections were collected of which 1446 were observed [$I/\sigma(I) > 2$]. Standard reflections $4\bar{2}\bar{2}$ and $2\bar{8}1$ showed no significant variation. The structure was solved by direct methods with the program *SHELXTL* (Sheldrick, 1981). H atoms were located in difference maps. 160 parameters were refined: atom coordinates, anisotropic temperature factors for all non-H atoms, isotropic temperature factors for H atoms; a maximum of 103 parameters refined each least-squares cycle with a subset of coordinates in each cycle. $R = 0.047$, unit weight, $(\Delta/\sigma)_{max} = 0.16 \times 10^{-4}$. Final difference Fourier synthesis $-0.34 < \Delta\rho < 0.84$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Atomic coordinates and isotropic thermal parameters are given in Table 1.* Bond lengths and angles

---

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54976 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.