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

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

	x	*y*	*z*	B_{eq}
O1	0.9740 (5)	0.2628 (6)	0.0957 (6)	5.91 (4)
O2	0.8125 (6)	0.5375 (7)	0.1544 (7)	7.86 (5)
C1	1.1089 (7)	0.1762 (8)	0.1242 (7)	4.66 (5)
C2	1.1805 (8)	0.0033 (8)	0.0839 (8)	5.68 (6)
C3	1.3105 (8)	−0.0611 (8)	0.1265 (9)	5.34 (6)
C4	1.3667 (6)	0.0457 (7)	0.2113 (7)	4.30 (5)
C5	1.2910 (7)	0.2192 (7)	0.2476 (7)	4.00 (5)
C6	1.1578 (6)	0.2902 (7)	0.2049 (7)	3.91 (5)
C7	1.0496 (6)	0.4611 (7)	0.2300 (7)	4.33 (5)
C8	0.9304 (8)	0.4357 (7)	0.1615 (9)	5.53 (6)
C9	1.0463 (6)	0.6157 (7)	0.2951 (7)	4.48 (5)
C10	1.1818 (7)	0.6236 (7)	0.3337 (8)	4.07 (4)
C11	1.1625 (8)	0.7307 (8)	0.4962 (8)	5.66 (6)
C12	1.2904 (11)	0.7367 (10)	0.5310 (9)	6.70 (7)
C13	1.4390 (9)	0.6420 (9)	0.4052 (10)	5.98 (6)
C14	1.4581 (7)	0.5413 (8)	0.2434 (8)	5.16 (6)
C15	1.3293 (7)	0.5321 (7)	0.2095 (8)	4.54 (5)
C16	0.9114 (8)	0.7863 (9)	0.3303 (9)	5.68 (6)
C17	1.5059 (7)	−0.0279 (8)	0.2559 (9)	6.10 (6)

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

C1—C2	1.363 (10)	C8—O1	1.369 (10)
C1—O1	1.388 (9)	C8—O2	1.213 (10)
C1—C6	1.385 (11)	C9—C10	1.470 (10)
C2—C3	1.378 (11)	C9—C16	1.509 (9)
C3—C4	1.407 (11)	C10—C11	1.395 (9)
C4—C5	1.378 (8)	C10—C15	1.373 (8)
C4—C17	1.477 (10)	C11—C12	1.378 (15)
C5—C6	1.414 (9)	C12—C13	1.385 (11)
C6—C7	1.442 (8)	C13—C14	1.372 (11)
C7—C8	1.492 (12)	C14—C15	1.393 (11)
C7—C9	1.349 (10)		
O1—C1—C2	124.6 (7)	C7—C8—O1	108.4 (6)
O1—C1—C6	110.8 (6)	C7—C8—O2	131.6 (8)
C2—C1—C6	124.5 (6)	O1—C8—O2	120.0 (8)
C1—C2—C3	117.2 (7)	C8—O1—C1	108.6 (6)
C2—C3—C4	122.1 (6)	C7—C9—C10	119.6 (5)
C3—C4—C5	118.3 (6)	C7—C9—C16	124.3 (6)
C3—C4—C17	120.5 (6)	C10—C9—C16	116.0 (6)
C5—C4—C17	121.2 (6)	C9—C10—C11	120.8 (5)
C4—C5—C6	121.3 (6)	C9—C10—C15	121.1 (6)
C5—C6—C1	116.5 (6)	C11—C10—C15	118.1 (7)
C5—C6—C7	135.6 (6)	C10—C11—C12	120.3 (5)
C1—C6—C7	107.8 (5)	C11—C12—C13	121.0 (7)
C6—C7—C8	104.3 (6)	C12—C13—C14	119.1 (8)
C6—C7—C9	132.2 (6)	C13—C14—C15	119.8 (6)
C8—C7—C9	123.5 (6)	C14—C15—C10	121.7 (6)
C1—C2—C3—C4	0.9 (4)	C10—O1—C11—C12	−2.6 (4)
C2—C3—C4—C5	0.2 (4)	C12—C13—C14—C15	−0.3 (3)
C3—C4—C5—C6	−0.6 (3)	C13—C14—C15—C16	−1.8 (7)
C4—C5—C6—C1	0.4 (4)	C14—C15—C16—C11	1.7 (6)
C5—C6—C1—C2	0.7 (3)	C15—C16—C11—C12	−180 (3)
C6—C1—C2—C3	−1.0 (3)	C16—C11—C12—C13	−2.8 (6)
C9—C10—O11—C11	3.2 (3)	C17—C14—C13—C12	178.6 (2)
C9—C12—C11—O1	−0.7 (5)	C16—C11—C12—C9	−175.3 (4)

Data were collected using a variable scan rate and a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. Data were corrected for Lorentz, polarization, centering and background effects (Blessing, 1986). The non-H atoms were located by direct methods using *MULTAN*80 (Main *et al.*, 1980). Refinement (*XRAY*; Stewart, 1980) of the scale factor and positional and anisotropic displacement parameters for these atoms was carried out to convergence. H atoms were located from a difference Fourier synthesis and were included in the final cycles of refinement in fixed positions and with fixed isotropic displacement parameters.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: SZ1043). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1-Bromo-2,7-dimethylnaphthalene

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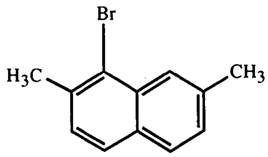
Abstract

The naphthalene moiety of the title compound, $C_{12}H_{11}Br$, is planar within 0.052 (4) Å. The Br, C11 and C12 atoms deviate by −0.1711 (5), 0.065 (5) and 0.182 (4) Å, respectively, from this plane. The C—Br distance is 1.911 (3) Å.

Comment

The bond lengths and angles (Table 2) within the aromatic nucleus of the title compound, (I), differ in some respects from those described by Cruickshank (1957) for naphthalene. The largest deviations occur where the ring is the most substituted, at atoms C1 and C2. The C1—C2 bond distance in the title compound is 0.029 (6) Å longer than that in naphthalene. The C2—C1—C9 angle is 3.2 (4)° larger, the C2—C3—C4 angle 2.8 (3)° larger, while the C1—C2—C3 angle is smaller by 4.3 (3)° than the corresponding angles in naphthalene. The largest deviation from the naphthalene (C1–C10) least-squares plane is observed at atom C12

[0.182 (4) Å], slightly larger than that of the Br atom [−0.1711 (5) Å] and nearly three times as large as that of C11 [0.065 (5) Å]. One would suspect atom C11 to be more inclined (as a result of the nearby bulky Br atom) to escape the naphthalene plane than atom C12, but the opposite seems to occur.



(I)

The shortest intermolecular contacts in the title compound [C3···C11′ 3.553 (6), C2···C11′ 3.623 (6) and C2···C2′ 3.685 (5) Å] are between adjacent molecules related by the inversion center at $(1, \frac{1}{2}, \frac{1}{2})$. These molecules are necessarily parallel, with their least-squares planes separated by 3.409 Å. They are not, however, stacked directly on top of each other (as are other 1,2,7-trisubstituted dimethylnaphthalenes). Instead, the two molecules are shifted by 6.267 Å from being stacked one on top of the other; the distance between their centroids being 7.134 Å. The crystal structures of several other 1,2,7-trisubstituted naphthalenes have been determined; 1-acetyl-2,7-dimethoxynaphthlene (Prince, Fronczek & Gandour, 1989), 1-(1-chlorovinyl)-2,7-dimethoxynaphthalene (Prince, Evans, Boss, Fronczek & Gandour, 1990), 1-ethynyl-2,7-dimethoxynaphthlene (Prince, Fronczek & Gandour, 1990), 1-acetyl-7-methoxy-2-naphthol (Prince, Fronczek & Gandour, 1992), and 2,7-dimethylnaphthalene-1-carbonitrile, 7-(dibromomethyl)-2-methylnaphthalene-1-carbonitrile and 2-(bromomethyl)-7-(dibromomethyl)naphthalene-1-carbonitrile (Brown, Fronczek & Maverick, 1996). The structure of 3-bromo-1,8-dimethylnaphthalene, an isomer of the title compound, has also been determined (Jameson & Penfold, 1965).

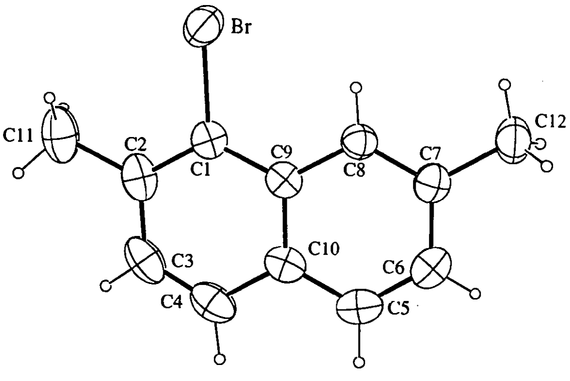


Fig. 1. Molecular structure of the title compound showing 40% probability ellipsoids. H atoms are illustrated by circles of arbitrary radii.

Experimental

The title compound was prepared as described by Clar & Wallenstein (1931). A higher yield was obtained by cooling the CS_2 solution to 273 K before adding Br_2. The mixture was allowed to warm to room temperature after the addition. After stirring at room temperature for 1 h, the CS_2 and any unreacted Br_2 were removed by evaporation at reduced pressure. The crude product was washed with hexane through a filter containing alumina, charcoal and Celite. After evaporation of the solvent, the remaining oil crystallized (yield 82%; m.p. 321–323 K). From this product, crystals were taken for X-ray analysis.

Crystal data

$C_{12}H_{11}Br$
$M_r = 235.13$
Monoclinic
$P2_1/c$
$a = 7.1790 (4)$ Å
$b = 7.8190 (4)$ Å
$c = 17.987 (2)$ Å
$\beta = 92.44 (1)°$
$V = 1008.8 (2)$ Å^3
$Z = 4$
$D_x = 1.546$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10–13°$
$\mu = 3.978$ mm^{-1}
$T = 295$ K
Lath fragment
0.57 × 0.55 × 0.10 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.3466$, $T_{\max} = 0.9998$
4907 measured reflections
3510 independent reflections

1979 observed reflections $[I > 1.0\sigma(I)]$
$R_{\rm int} = 0.022$
$\theta_{\max} = 32°$
$h = 0 \rightarrow 10$
$k = -7 \rightarrow 11$
$l = -26 \rightarrow 26$
3 standard reflections
frequency: 60 min
intensity decay: 6.80%

Refinement

Refinement on F
$R = 0.058$
$wR = 0.042$
$S = 1.657$
1979 reflections
139 parameters
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0004F_o^4]$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.697$ e Å^{-3}
$\Delta\rho_{\min} = -0.302$ e Å^{-3}

Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: $0.15 (7) \times 10^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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	$U_{\rm eq}$
Br	0.64565 (5)	0.18265 (6)	0.46755 (2)	0.0613 (1)
C1	0.8411 (4)	0.2765 (4)	0.4113 (2)	0.0441 (9)
C2	1.0143 (4)	0.2991 (5)	0.4470 (2)	0.054 (1)
C3	1.1518 (4)	0.3774 (5)	0.4049 (2)	0.063 (1)

C4	1.1210 (4)	0.4289 (5)	0.3344 (2)	0.062 (1)
C5	0.9089 (4)	0.4475 (5)	0.2222 (2)	0.057 (1)
C6	0.7429 (5)	0.4112 (5)	0.1866 (2)	0.057 (1)
C7	0.6012 (4)	0.3270 (5)	0.2237 (2)	0.0479 (8)
C8	0.6305 (4)	0.2868 (4)	0.2972 (2)	0.0435 (9)
C9	0.8016 (4)	0.3206 (4)	0.3365 (2)	0.0409 (8)
C10	0.9453 (4)	0.4013 (5)	0.2972 (2)	0.0483 (9)
C11	1.0600 (6)	0.2471 (6)	0.5263 (2)	0.074 (1)
C12	0.4233 (5)	0.2796 (6)	0.1815 (2)	0.064 (1)

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

Br—C1	1.911 (3)	C5—C6	1.359 (5)
C1—C2	1.386 (4)	C5—C10	1.409 (5)
C1—C9	1.405 (5)	C6—C7	1.405 (5)
C2—C3	1.409 (5)	C7—C8	1.365 (5)
C2—C11	1.505 (6)	C7—C12	1.504 (5)
C3—C4	1.341 (6)	C8—C9	1.417 (4)
C4—C10	1.419 (4)	C9—C10	1.423 (4)
Br—C1—C2	117.9 (3)	C6—C7—C8	118.9 (3)
Br—C1—C9	118.6 (2)	C6—C7—C12	119.5 (3)
C2—C1—C9	123.5 (3)	C8—C7—C12	121.6 (3)
C1—C2—C3	116.2 (3)	C7—C8—C9	122.4 (3)
C1—C2—C11	124.0 (3)	C1—C9—C8	124.6 (3)
C3—C2—C11	119.8 (3)	C1—C9—C10	117.7 (3)
C2—C3—C4	123.3 (3)	C8—C9—C10	117.7 (3)
C3—C4—C10	120.5 (3)	C4—C10—C5	122.5 (3)
C6—C5—C10	121.4 (3)	C4—C10—C9	118.8 (3)
C5—C6—C7	120.8 (3)	C5—C10—C9	118.7 (3)

The structure was solved by Patterson and Fourier methods. Initially, data were collected using a weakly scattering crystal and Cu $K\alpha$ radiation. The structure was solved using these data, but the refinement did not yield satisfactory results. A crystal was found which scattered strongly and Mo $K\alpha$ radiation was chosen to collect data from this crystal to take advantage of the lower absorption and higher resolution available. The Mo $K\alpha$ data collection crystal was sealed in a capillary to prevent sublimation. Ring H atoms were refined isotropically, while methyl H atoms were placed in calculated positions (C—H 0.95 Å), guided by difference maps. R = 0.038 for 1499 data having $I > 3\sigma(I)$.

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual.* Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to refine structure: *MolEN LSFM.* Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN CIF IN.*

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1195). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-(Phosphonomethyl)acrylic Acid Hemihydrate and Ammonium 2-(Phosphonomethyl)acrylate: Analogues of Phosphoenolpyruvate (PEP)

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Abstract

The structures of hydrated 2-(phosphonomethyl)acrylic acid, $C_4H_7O_5P.0.5H_2O$, (I), and its ammonium salt, $NH_4^+.C_4H_6O_5P^-$, (II), are described. In (I), the two crystallographically independent 2-(phosphonomethyl)acrylic acid residues differ slightly in the orientation of the phosphonic group relative to the rest of the molecule. In both compounds, the phosphonic group projects out the plane of the 2-methyleneacrylate system. The carboxylic hydroxyl is *trans* planar to the terminal $=CH_2$ group in (II) but is *syn* planar in (I). In both crystals, all OH and NH groups are involved in intermolecular hydrogen bonds.

Comment

Numerous phosphoenolpyruvate (PEP) analogues are used for the study of enzyme-catalyzed reactions (Stubbe & Kenyon, 1972; Wirsching & O'Leary, 1988; Sikkema & O'Leary, 1988). 2-(Phosphonomethyl)acrylic acid, a phosphonate analogue of PEP in which