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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1050). Services for accessing these data are described at the back of the journal.

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(*tert*-Butoxycarbonylamino)acetonitrile†

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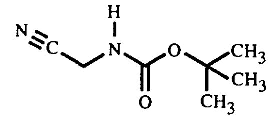
Abstract

The title compound, $C_7H_{12}N_2O_2$, is a useful intermediate for the synthesis of peptidic nucleic acids containing a backbone composed of repeating (2-aminoethyl)glycine units. Conjugation within the urethane system is facilitated by near planarity about both C—O and C—N bonds. There is a synperiplanar relationship between the O11 atom of the carbonyl group and the tertiary C7 atom, along with an antiperiplanar relationship between the C5 atom and the C10 methyl group.

Comment

Peptidic nucleic acids (PNAs) are useful nucleic acid mimetics which contain aminoethylglycine units in place of the conventional DNA sugar–phosphate backbone (Hyrup & Nielsen, 1996). PNAs containing the usual DNA bases (Egholm *et al.*, 1993) along with pseudoisocytosine (Egholm *et al.*, 1995) possess antisense/antigene properties (Noble *et al.*, 1995; Knudsen & Nielsen, 1996). Our interest in modulating the hydrogen-bonding interactions between PNA and DNA oligomers prompted an investigation of PNAs containing other purine bases such as xanthine and diaminopurine. The title compound, (1), is a key intermediate for the synthesis of the PNA backbone structure (Meltzer, Liang & Matsudaira, 1995; Ravikumar, 1994) which is available as an oil through acylation of aminoacetonitrile hydrochloride using di-Boc anhydride or on dehydration of 3-(*tert*-Boc-amino)ethanamide (Houssin, Bernier & Heinichart, 1988) (where Boc is butoxycarbonyl). We have successfully prepared (1) in crystalline form for the first time and here we compare its crystal structure with that of other Boc-protected analogues.



(1)

In common with other urethanes, the O6—C5—N4 bond angle is approximately 10° lower than the trigonal value. The *trans* orientation of the O11 atom compared to the H atom attached to N4 is a general feature among Boc-protected amino acids. Like Boc-protected glycine (Semertzidis *et al.*, 1989) and alanine (Benedetti *et al.*, 1981) structures, (1) has a synperiplanar relationship about the C5—O6 bond between the carbonyl O11 atom and the tertiary C7 atom, as well as an antiperiplanar disposition of one methyl group (C10) to the carbonyl C5 atom. However, the locations of the multiply bonded C atom, C2, in (1) and the carboxyl C atom in the amino acids, show more variability: C2—C3—N4—C5 is (−)-synclinal in (1) but ranges from 62.9 to 110.7° in the latter. N4, the only proton donor group, donates a fairly weak intermolecular hydrogen bond to a nearby N1 atom related by $(2 - x, -0.5 + y, 0.5 - z)$ with H4···N1 2.37 (2) Å and N4···N1 3.132 (2) Å.

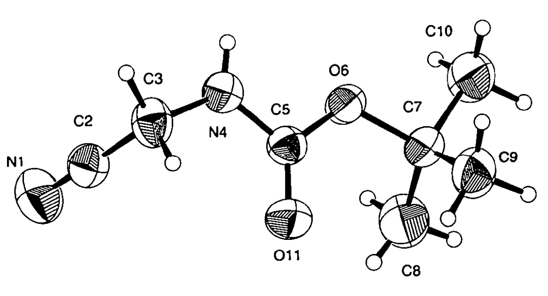


Fig. 1. *ORTEP*II view (Johnson, 1976) of the molecule. Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as small spheres of arbitrary radius.

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† Alternative name: *tert*-butyl 3-cyano-2-azapropanoate.

Experimental

To a mixture of aminoacetonitrile hydrochloride (30.0 g, 0.325 mol) and di-Boc anhydride (70.9 g, 0.325 mol) in CH_2Cl_2 (1 l), Et_3N (125 ml, 0.9 mol) was added dropwise and the mixture stirred overnight at room temperature. After rotary evaporation of the product mixture, the residue was dissolved in ether, washed with water followed by brine and then dried ($MgSO_4$). Evaporation of the solvent gave the title compound (43.3 g, 85%). Recrystallization from EtOAc gave the analytical sample (m.p. 328–331 K). Thin-layer chromatography (EtOAc) R_f 0.58. IR (KBr disc): ν_{max} 3390, 3010, 2995, 2252, 1720, 1534, 935, 839, 783 cm^{-1} (all strong bands). ^1H NMR [250.1 MHz; ($CDCl_3$)]: δ 1.46 [*s*, 9 H, $(CH_3)_3$], 4.05 (*d*, 2 H, *J* = 6.0 Hz, CH_2), 5.30 p.p.m. (*m*, 1 H, NH, D_2O exchangeable). ^{13}C NMR [250.1 MHz; ($CDCl_3$)]: δ 28.1 $(CH_3)_3$, 29.0 (CH_2), 81.1 (C), 115.6 (CN), 155.0 p.p.m. (CO). MS (CI^+): *m/z* (I_r) 157 (M^+H, 93%), 118 (100%), 74 (26%), 72 (6%), 56 (8%); Analysis calculated for $C_7H_{12}N_2O_2$: C 53.8, H 7.7, N 17.9%. Found: C 53.8, H 7.6, N 17.8%.

Crystal data

$C_7H_{12}N_2O_2$
$M_r = 156.19$
Orthorhombic
$P2_12_12_1$
$a = 8.5261 (7)$ Å
$b = 10.0120 (7)$ Å
$c = 10.2216 (14)$ Å
$V = 872.5 (2)$ Å^3
$Z = 4$
$D_x = 1.189$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 22.7–29.1°$
$\mu = 0.729$ mm^{-1}
$T = 293 (2)$ K
Tabular
0.6 × 0.6 × 0.2 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.788$, $T_{max} = 0.864$
1862 measured reflections
1658 independent reflections

1624 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0255$
$\theta_{max} = 69.91°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 12$
$l = -12 \rightarrow 12$
3 standard reflections frequency: 120 min intensity decay: 14%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0286$
$wR(F^2) = 0.0843$
$S = 1.084$
1658 reflections
149 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0586P)^2 + 0.0396P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$

$\Delta\rho_{max} = 0.10$ e Å^{-3}
$\Delta\rho_{min} = -0.09$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.095 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.5 (2)

Table 1. *Selected geometric parameters (Å, °)*

N1—C2	1.134 (2)	C5—O6	1.3400 (14)
C2—C3	1.471 (2)	O6—C7	1.4774 (13)
C3—N4	1.436 (2)	C7—C8	1.514 (2)
N4—C5	1.354 (2)	C7—C10	1.515 (2)
C5—O11	1.2090 (15)	C7—C9	1.511 (2)
N1—C2—C3	177.7 (2)	O6—C7—C8	110.13 (11)
N4—C3—C2	112.50 (11)	O6—C7—C10	102.34 (10)
C5—N4—C3	120.07 (11)	C8—C7—C10	112.11 (14)
O11—C5—O6	126.77 (11)	O6—C7—C9	109.64 (11)
O11—C5—N4	123.50 (11)	C8—C7—C9	112.93 (14)
O6—C5—N4	109.73 (9)	C10—C7—C9	109.16 (12)
C5—O6—C7	120.76 (9)		
C2—C3—N4—C5	−84.25 (15)	C5—O6—C7—C10	−178.53 (11)
O11—C5—O6—C7	−2.5 (2)		

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CADABS* (Gould & Smith, 1996). Program(s) used to solve structure: *MULTAN*11/84 (Main, Germain & Woolfson, 1984). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1121). Services for accessing these data are described at the back of the journal.

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Isotopically Substituted Bis(ethylenedithio)tetrathiafulvalene at 15 K by Time-of-Flight Neutron Diffraction

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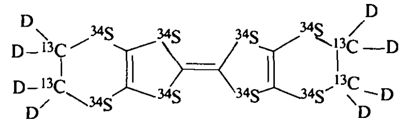
Abstract

The title compound, $C_{10}D_8S_8$, (ET), has been synthesized whereby all eight S atoms, the four ethylene C atoms and all eight H atoms have been isotopically substituted with ^{34}S, ^{13}C and ^{2}H, respectively. Analysis of the neutron scattering lengths derived from single-crystal time-of-flight neutron diffraction data obtained at T = 15 K confirms the isotopic distribution. The title phase crystallizes in the space group $P2_1/n$ with bond lengths and angles consistent with neutral ET.

Comment

The title compound, (I), (ET), participates as the electron-donor molecule in a large number of organic superconducting salts (Williams *et al.*, 1991). In order to investigate the mechanism for the electron pairing in this class of superconductors, a variety of isotopically substituted ET molecules with different distributions of isotopes throughout the molecule have been synthesized (Kini *et al.*, 1996). Salts of these organic donor molecules have been studied to determine the isotopic effect on T_c in the superconducting crystals. In the crystal used in this neutron diffraction experiment, the isotopic substitution of the ET molecule involved the replacement of the four C atoms in the terminal 1,2-ethanediyl groups with ^{13}C, all eight S atoms with ^{34}S and all eight H atoms with deuterium, ^{2}H. The substitution increases the mass of the ET molecule, hereafter denoted by $^{2}H_8{}^{13}C_4{}^{34}S_8$–ET, by 28 a.m.u., which is about 7% of the original mass. From the study by Kini *et al.* (1996), it was shown that the C and S substitution has a normal BCS-like mass (M) effect (T_c proportional to $M^{-\alpha}$), whereas deuterium substitution produces an inverse isotopic effect (T_c increases). We present here the neutron structure of $^{2}H_8{}^{13}C_4{}^{34}S_8$–ET at 15 K in order to confirm the isotopic distribution and to provide high-precision low-temperature structural parameters.



(I)

The only previous structure of neutral ET is the room-temperature single-crystal X-ray structure in space group $P2_1/c$ by Kobayashi, Kobayashi, Yukiyoshi, Saito & Inokuchi (1986). We had transformed the atomic coordinates from $P2_1/c$ to $P2_1/n$ in our previous comparison of the ET structure with the isomorphous $Au(DDDT)_2$ (DDDT = 5,6-dihydro-1,4-dithiin-2,3-dithiolate) crystal structure (Schultz *et al.*, 1987). The transformation of the atomic coordinates from the $P2_1/c$ unit cell in Kobayashi *et al.* (1986) to the $P2_1/n$ unit cell in this paper is $(x - z, -y, -z) + (1/2, 1/2, 0)$.

The $P2_1/n$ room-temperature unit cell of neutral ET reported by Kobayashi *et al.* (1986) is a = 6.614 (11), b = 13.985 (2), c = 15.721 (3) Å, β = 93.81 (2)° and V = 1451 (5) Å^3. The low-temperature data of isotopically substituted ET gave a slightly smaller volume, as expected, of 1416 (1) Å^3 and a = 6.661 (1), b = 13.652 (2), c = 15.613 (2) Å, β = 94.281 (2)°. The bond lengths of the low-temperature isotopically substituted ET appear to be slightly longer than those obtained from room-temperature data. Shorter bond distances of the room-temperature neutral ET are probably attributable to anisotropic thermal motion. Isotopically substituted ET bond distances at 15 K are C1—C2 = 1.359 (2), C5—C6 = 1.360 (2), S2—C4 = 1.771 (3) and S4—C6 = 1.769 (3) Å. Kobayashi *et al.* (1986) reported 1.319, 1.328, 1.757 and 1.751 ± (0.007–0.012) Å, respectively.

The ET molecules pack as face-to-face dimeric pairs. Many of the S—S contacts between different molecules have distances close to the sum of the van der Waals radii (3.70 Å). The S···S contacts are listed in Table 2.

The crystal for this data collection was obtained from a batch of crystals which underwent mass spectrometry to verify isotopic substitution. In order to confirm the degree of isotopic substitution of this crystal, scattering lengths for each of the atoms were refined. Scattering lengths in units of 10^{-12} cm from Sears (1986) are: $b(^{12}C)$ = 0.66511 (16), $b(^{13}C)$ = 0.619 (9), $b(^{32}S)$ = 0.2804 (2), $b(^{34}S)$ = 0.348 (3), b(H) = −0.37406 (11), b(D) = 0.6671 (4). The average refined scattering length in this structure of the ethanediyl ^{13}C atoms is 0.656 (3) × 10^{-12} cm, which appears to be closer in magnitude to ^{12}C but is also within three standard deviations of the ^{13}C scattering length. Thus, the refined ethanediyl