

References

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Dipyridiniummethane 1-Iodo-*closo*-decaborate, [(C₅H₅N)₂CH₂][1-IB₁₀H₉]²⁻

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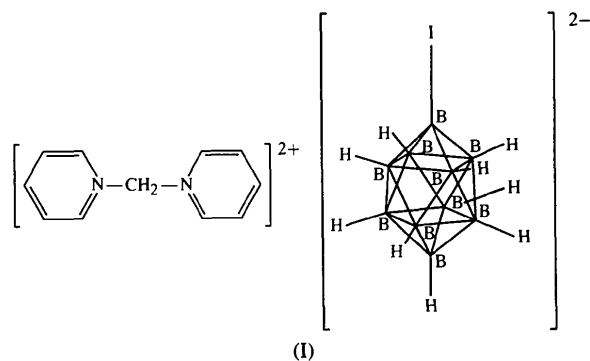
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Abstract

The structure of the title compound [*N,N'*-methylene-dipyridinium 1-iodononahydro-*closo*-decaborate(2-), C₁₁H₁₂N₂²⁺·B₁₀H₉I²⁻] has been determined by single-crystal X-ray diffraction at room temperature. This is the first halogeno derivative of *closo*-[B₁₀H₁₀]²⁻ with the substituent in the apical position. The square pyramid with the capping *ipso*-B atom is slightly compressed. The B—I distance of 2.209 (6) Å in [1-IB₁₀H₉]²⁻ is significantly shorter than the distance of 2.230 (2) Å in the [2-IB₁₀H₉]²⁻ isomer.

Comment

As part of our work on *closo*-borates we are interested in derivatives of [B₁₀H₁₀]²⁻ and the sequence of substituting reactions. By treatment with chlorine, bromine and iodine, compounds of the type *closo*-[2-*XB*₁₀H₉]²⁻ (*X* = Cl, Br, I) are formed, which have been characterized by ¹¹B and ¹¹B(¹H) NMR, and vibrational spectroscopy (Pretz, Srebný & Marsmann, 1984) as well as by X-ray studies (Pretz & Nachtigal, 1995). After iodination, the isomeric species [1-IB₁₀H₉]²⁻, substituted in an apical position of the B₁₀ cage, could be isolated from the reaction mixture in minor yield. Using the dipyridiniummethane dication (Brüdgam & Hartl, 1986), the *AB*-type salt [(C₅H₅N)₂CH₂][1-IB₁₀H₉], (I), was precipitated from aqueous solution as single crystals.



A view of (I) with the atom labelling is shown in Fig. 1. The cluster anion has *C*_{4v} point symmetry and features three types of B—B distances. Bonds from the capping atoms B1 and B10 to the upper base (B2–B5) and the lower base (B6–B9), respectively, are the same to within the standard deviations with a mean value of 1.685 Å. The average B—B bond length within the bases is 1.830 Å and the average length of the connecting bonds between the bases is 1.793 Å. The upper square pyramid is slightly compressed compared with the lower square pyramid: the *ipso*-B1 distance to the B2–B5 plane is 1.065 Å whereas the antipodal B10 to B6–B9 base distance is 1.091 Å (Roberts & Sheldrick, 1975). The I—B1 distance in [1-IB₁₀H₉]²⁻ of 2.209 (6) Å is in the same range as that found for similar *closo*-borates with the *ipso*-B atoms bonded to four other B atoms, for example [B₆H₆I]⁻ [2.174 (3) Å; Pretz & Sonnack, 1994] and [B₆I₆]²⁻ (2.18 Å; Heinrich, Keller & Pretz, 1990). The B—I distance is significantly lengthened if the *ipso*-B atom is connected to five other B atoms as in [2-IB₁₀H₉]²⁻ [2.230 (2) Å; Pretz & Nachtigal, 1995] and [IB₁₂H₁₁]²⁻ [2.226 (4) Å; Haeckel & Pretz, 1995].

The [(C₅H₅N)₂CH₂]²⁺ dication is bent by the N1—CM—N2 angle of 112.3 (5)° and the normals of the pyridine rings form an angle of 74.4 (4)° (Roberts &

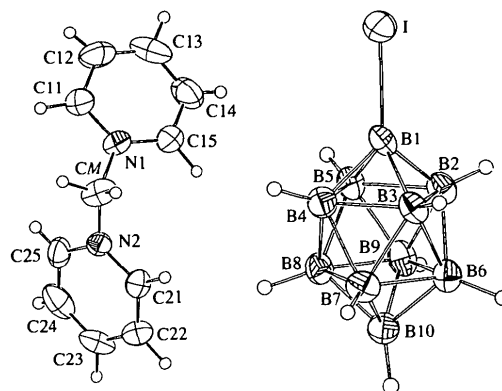
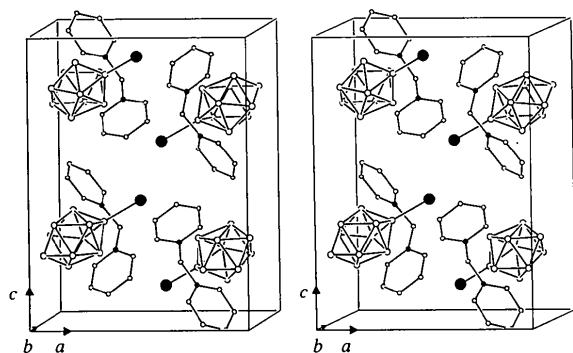


Fig. 1. View of the [(C₅H₅N)₂CH₂]²⁺ cation and [1-IB₁₀H₉]²⁻ anion. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms; H atoms are drawn as spheres of arbitrary radii.

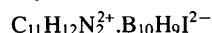
Fig. 2. Stereoview of the packing along *b*.

Sheldrick, 1975). In the monoclinic unit cell the cations are orientated with respect to the B₁₀ cages like opened mussels, as shown by the stereoview in Fig. 2.

Experimental

[B₁₀H₉I]²⁻ reacts with iodine yielding the monoiodo-decaborates [1-IB₁₀H₉]²⁻ (30%) and [2-IB₁₀H₉]²⁻ (70%), which are separated by ion-exchange chromatography on diethylaminoethyl (DEAE) cellulose from the starting compound and higher iodated products (Pretz, Srebny & Marsmann, 1984). [(C₅H₅N)₂CH₂][1-IB₁₀H₉] was precipitated from a solution of Cs₂[1-IB₁₀H₉] in water with dipyridinomethane dibromide and recrystallized from water/ether to give yellow single crystals.

Crystal data

*M_r* = 416.30

Monoclinic

*P*2₁/*c**a* = 11.3140 (6) Å*b* = 10.8720 (10) Å*c* = 14.740 (2) Å

β = 90.369 (7)°

V = 1813.1 (3) Å³*Z* = 4*D_x* = 1.525 Mg m⁻³

Mo Kα radiation

λ = 0.71069 Å

Cell parameters from 25 reflections

θ = 5.53–10.39°

μ = 1.759 mm⁻¹*T* = 293 (2) K

Prismatic

0.3 × 0.2 × 0.2 mm

Yellow

Data collection

Enraf–Nonius CAD-4-Turbo diffractometer

ω/2θ scans

Absorption correction:

empirical via ψ scans

(North, Phillips & Mathews, 1968)

T_{min} = 0.8046, *T_{max}* = 0.9991

3358 measured reflections

3187 independent reflections

2208 observed reflections

[*I* > 2σ(*I*)]*R_{int}* = 0.0372θ_{max} = 24.99°*h* = 0 → 13*k* = 0 → 12*l* = -17 → 17

3 standard reflections

frequency: 240 min

intensity decay: 1.1%

Refinement

Refinement on *F*²*R*[*F*² > 2σ(*F*²)] = 0.0350*wR*(*F*²) = 0.0992(Δ/σ)_{max} = 0.001Δρ_{max} = 0.933 e Å⁻³Δρ_{min} = -0.521 e Å⁻³*S* = 1.189

3186 reflections

301 parameters

All H-atom parameters

refined

w = 1/[σ²(*F_o*²) + (0.0300*P*)²+ 3.5356*P*]where *P* = (*F_o*² + 2*F_c*²)/3

Extinction correction: none

Atomic scattering factors

from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
<i>CM</i>	0.3268 (7)	0.1943 (7)	0.2064 (5)	0.053 (2)
<i>N1</i>	0.2497 (4)	0.1638 (4)	0.1291 (3)	0.0389 (11)
<i>N2</i>	0.3186 (4)	0.1049 (4)	0.2789 (3)	0.0361 (11)
<i>C11</i>	0.1573 (6)	0.2367 (7)	0.1096 (4)	0.050 (2)
<i>C12</i>	0.0881 (6)	0.2094 (9)	0.0355 (5)	0.061 (2)
<i>C13</i>	0.1124 (8)	0.1101 (8)	-0.0170 (5)	0.067 (2)
<i>C14</i>	0.2054 (10)	0.0367 (8)	0.0057 (5)	0.076 (3)
<i>C15</i>	0.2742 (7)	0.0656 (7)	0.0785 (5)	0.058 (2)
<i>C21</i>	0.4086 (5)	0.0280 (6)	0.2955 (4)	0.0392 (14)
<i>C22</i>	0.4044 (5)	-0.0533 (6)	0.3648 (4)	0.0448 (15)
<i>C23</i>	0.3068 (6)	-0.0569 (7)	0.4184 (4)	0.053 (2)
<i>C24</i>	0.2159 (7)	0.0200 (9)	0.4007 (5)	0.063 (2)
<i>C25</i>	0.2216 (6)	0.1015 (7)	0.3315 (5)	0.050 (2)
<i>I</i>	0.47998 (3)	-0.20614 (4)	0.08838 (3)	0.04697 (15)
<i>B1</i>	0.3251 (5)	-0.2894 (7)	0.1550 (4)	0.0338 (13)
<i>B2</i>	0.1868 (5)	-0.3067 (6)	0.1139 (4)	0.0326 (13)
<i>B3</i>	0.2774 (6)	-0.4344 (7)	0.1556 (4)	0.0355 (15)
<i>B4</i>	0.3107 (5)	-0.3473 (6)	0.2594 (4)	0.0345 (14)
<i>B5</i>	0.2192 (5)	-0.2194 (6)	0.2167 (4)	0.0352 (14)
<i>B6</i>	0.1179 (6)	-0.4432 (6)	0.1573 (5)	0.0369 (15)
<i>B7</i>	0.2052 (6)	-0.4735 (6)	0.2597 (4)	0.0346 (14)
<i>B8</i>	0.1642 (6)	-0.3218 (6)	0.3042 (4)	0.037 (2)
<i>B9</i>	0.0774 (5)	-0.2929 (7)	0.2013 (4)	0.0350 (13)
<i>B10</i>	0.0641 (6)	-0.4231 (6)	0.2634 (5)	0.039 (2)

Table 2. Selected geometric parameters (Å, °)

<i>I</i> — <i>B1</i>	2.209 (6)	<i>B4</i> — <i>B7</i>	1.819 (9)
<i>B1</i> — <i>B3</i>	1.666 (10)	<i>B4</i> — <i>B5</i>	1.842 (9)
<i>B1</i> — <i>B4</i>	1.671 (9)	<i>B5</i> — <i>B9</i>	1.806 (9)
<i>B1</i> — <i>B2</i>	1.685 (8)	<i>B5</i> — <i>B8</i>	1.816 (9)
<i>B1</i> — <i>B5</i>	1.690 (8)	<i>B6</i> — <i>B10</i>	1.696 (9)
<i>B2</i> — <i>B6</i>	1.796 (10)	<i>B6</i> — <i>B9</i>	1.817 (9)
<i>B2</i> — <i>B9</i>	1.798 (8)	<i>B6</i> — <i>B7</i>	1.828 (9)
<i>B2</i> — <i>B5</i>	1.823 (9)	<i>B7</i> — <i>B10</i>	1.689 (9)
<i>B2</i> — <i>B3</i>	1.830 (9)	<i>B7</i> — <i>B8</i>	1.835 (9)
<i>B3</i> — <i>B7</i>	1.794 (9)	<i>B8</i> — <i>B10</i>	1.687 (9)
<i>B3</i> — <i>B6</i>	1.808 (9)	<i>B8</i> — <i>B9</i>	1.829 (9)
<i>B3</i> — <i>B4</i>	1.836 (9)	<i>B9</i> — <i>B10</i>	1.693 (9)
<i>B4</i> — <i>B8</i>	1.809 (9)		
<i>N2</i> — <i>CM</i> — <i>N1</i>	112.3 (5)	<i>B2</i> — <i>B1</i> — <i>I</i>	128.6 (4)
<i>B3</i> — <i>B1</i> — <i>I</i>	130.4 (4)	<i>B5</i> — <i>B1</i> — <i>I</i>	128.4 (4)
<i>B4</i> — <i>B1</i> — <i>I</i>	130.2 (4)		

Data collection: *CAD-4-PC* (Enraf–Nonius, 1994). Cell refinement: *CAD-4-PC*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1085). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1-(4-Iodobenzoyl)-5-methoxy-2-methyl-3-indoleacetic Acid, an Iodinated Indomethacin Analog

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Abstract

The crystal structure of 1-(4-iodobenzoyl)-5-methoxy-2-methyl-3-indoleacetic acid, C₁₉H₁₆INO₄, an analog of indomethacin, is reported. Bond distances and angles in the title compound closely resemble those reported for indomethacin and reflect the presence of steric strain at the site of the linkage between the 4-iodobenzoyl group

and the indole moiety. The orientation of the 4-iodobenzoyl group with respect to the indole ring is not the same in the title compound as it is in indomethacin; the two structures are related by a rotation of 186° about the C2—N1—C10—C11 torsion angle.

Comment

Indomethacin is a well studied member of the class of compounds known as the nonsteroidal anti-inflammatory drugs (NSAIDs). In the course of our studies of the interactions of NSAIDs with their target, prostaglandin H₂ synthase, we synthesized the title compound, (I), an indomethacin analog. The IC₅₀ value of (I) for inhibition of the cyclooxygenase activity of prostaglandin H₂ synthase is roughly threefold lower than that of indomethacin. We have recently determined a low-resolution structure of (I) complexed with its target, allowing us to elucidate its mode of binding (Loll, Picot, Ekabo & Garavito, 1995).

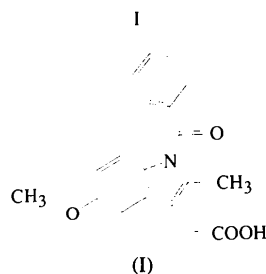


Fig. 1 shows a perspective view of the title compound. Evidence for steric strain is seen at the point where the 4-iodobenzoyl group joins the indole ring. The carbonyl group, comprising atoms O1 and C10, is prevented from lying in the plane of the indole ring by the close approach of O1 and the H atom bound to C8. The torsion angle C2—N1—C10—C11 is $-35.0(8)^\circ$;

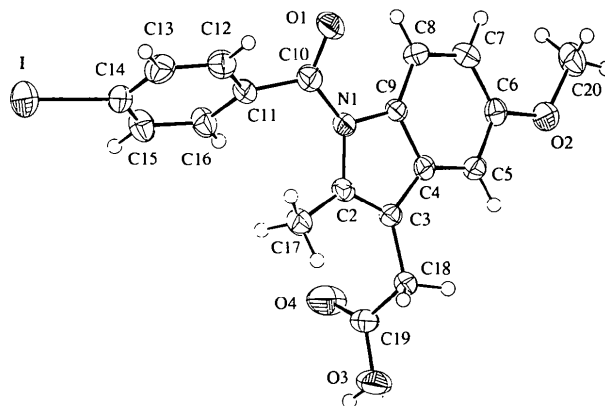


Fig. 1. View of the title compound showing the atomic labeling scheme (ORTEPII; Johnson, 1976). Displacement ellipsoids for non-H atoms are plotted at the 50% probability level and H atoms are drawn as spheres of arbitrary radii.