Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	*y*	*z*	U_{eq}
S(1)	0.1076 (1)	−0.1427 (1)	1.3884 (1)	0.041 (1)
S(2)	0.5952 (1)	−0.1049 (1)	1.3180 (1)	0.046 (1)
S(3)	−0.0274 (1)	0.0863 (1)	1.1767 (1)	0.037 (1)
S(4)	0.3841 (1)	0.1086 (1)	1.1168 (1)	0.034 (1)
S(5)	−0.2257 (1)	0.3177 (1)	0.9555 (1)	0.039 (1)
S(6)	0.1808 (1)	0.3495 (1)	0.8836 (1)	0.036 (1)
N(1)	−0.5495 (4)	0.5706 (4)	0.7156 (2)	0.054 (1)
N(2)	−0.0050 (4)	0.6262 (4)	0.6095 (2)	0.050 (1)
C(1)	0.3162 (4)	−0.1507 (5)	1.4683 (2)	0.040 (1)
C(2)	0.5285 (4)	−0.2472 (4)	1.4340 (2)	0.040 (1)
C(3)	0.1778 (4)	−0.0299 (4)	1.2701 (2)	0.029 (1)
C(4)	0.3630 (4)	−0.0176 (4)	1.2432 (2)	0.030 (1)
C(5)	0.1232 (4)	0.1653 (4)	1.0797 (2)	0.028 (1)
C(6)	0.0395 (4)	0.2638 (4)	0.9848 (2)	0.029 (1)
C(7)	−0.2142 (4)	0.4343 (4)	0.8283 (2)	0.030 (1)
C(8)	−0.0297 (4)	0.4493 (3)	0.7953 (2)	0.028 (1)
C(9)	−0.3984 (4)	0.5105 (4)	0.7643 (2)	0.035 (1)
C(10)	−0.0095 (4)	0.5468 (4)	0.6923 (2)	0.033 (1)

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

S(1)—C(1)	1.802 (3)	S(1)—C(3)	1.749 (2)
S(2)—C(2)	1.805 (3)	S(2)—C(4)	1.754 (2)
S(3)—C(3)	1.759 (2)	S(3)—C(5)	1.752 (2)
S(4)—C(4)	1.765 (2)	S(4)—C(5)	1.755 (2)
S(5)—C(6)	1.761 (3)	S(5)—C(7)	1.740 (2)
S(6)—C(6)	1.764 (2)	S(6)—C(8)	1.739 (2)
N(1)—C(9)	1.140 (4)	N(2)—C(10)	1.137 (3)
C(1)—C(2)	1.513 (4)	C(3)—C(4)	1.334 (4)
C(5)—C(6)	1.350 (3)	C(7)—C(8)	1.357 (4)
C(7)—C(9)	1.421 (3)	C(8)—C(10)	1.429 (3)
C(1)—S(1)—C(3)	99.3 (1)	N(1)—C(9)—C(7)	177.9 (3)
C(3)—S(3)—C(5)	95.5 (1)	C(2)—S(2)—C(4)	101.7 (1)
C(6)—S(5)—C(7)	94.2 (1)	C(4)—S(4)—C(5)	94.9 (1)
S(1)—C(1)—C(2)	113.3 (2)	C(6)—S(6)—C(8)	94.4 (1)
S(2)—C(2)—C(1)	113.6 (2)	S(1)—C(3)—C(4)	128.5 (2)
S(1)—C(3)—S(3)	114.4 (1)	S(2)—C(4)—S(4)	113.3 (1)
S(3)—C(3)—C(4)	117.0 (2)	S(4)—C(4)—C(3)	117.7 (2)
S(2)—C(4)—C(3)	129.0 (2)	S(3)—C(5)—C(6)	121.2 (2)
S(3)—C(5)—S(4)	114.8 (1)	S(5)—C(6)—S(6)	115.6 (1)
S(4)—C(5)—C(6)	124.0 (2)	S(6)—C(6)—C(5)	123.7 (2)
S(5)—C(6)—C(5)	120.7 (2)	S(5)—C(7)—C(9)	118.5 (2)
S(5)—C(7)—C(8)	118.2 (2)	S(6)—C(8)—C(7)	117.5 (2)
C(8)—C(7)—C(9)	123.3 (2)	C(7)—C(8)—C(10)	121.4 (2)
S(6)—C(8)—C(10)	121.1 (2)	N(2)—C(10)—C(8)	176.1 (3)

The structure was solved by direct methods and subsequent difference Fourier techniques, and refined by full-matrix least-squares methods with anisotropic displacement parameters for all non-H atoms. H atoms were found by difference Fourier techniques. All calculations were performed using the *SHELXTL/PC* system of computer programs (Sheldrick, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1079). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4-Chloro-7-(iodoacetyl)amino-3-methoxyisocoumarin

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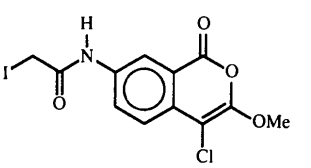
Abstract

The crystal structure of the iodo analog of 7-(bromoacetyl)amino-4-chloro-3-methoxyisocoumarin, an inhibitor of human neutrophil elastase (HNE), $C_{12}H_9ClINO_4$, has been determined. The isocoumarin ring system is highly planar, with the carbonyl group of the amide function being coplanar with the isocoumarin ring.

Comment

The title compound, (I), was synthesized from 7-amino-4-chloro-3-methoxyisocoumarin by known methods (Harper & Powers, 1985) using iodoacetic anhydride as the acylating agent. The bromo analog is an effective *in vitro* inhibitor of human neutrophil elastase (HNE) (Kerrigan, Oleksyszyn, Kam, Selzler & Powers, 1995). The title compound was synthesized to obtain a precise structure of an isocoumarin for future modeling studies in order to investigate further the inhibitory activity of the isocoumarins.



(I)

The isocoumarin ring system is planar [maximum displacement 0.024 (10) Å] with the carbonyl O(11) atom positioned slightly out-of-plane. The acetyl amide

C(17)—C(16)[=O(19)]—N(15) group is coplanar with the ring system, as is the methoxy O(12)—C(13) group. The iodo group I(18)—C(17) is positioned orthogonal to the ring system, with the I atom 1.850 (8) Å from the least-squares plane.

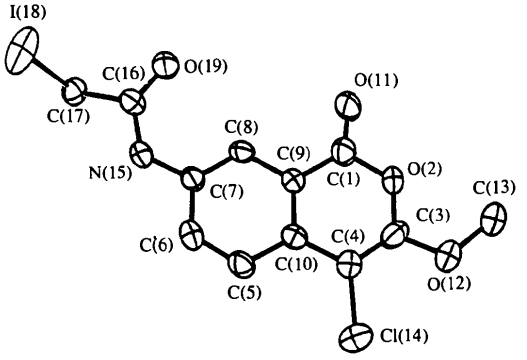


Fig. 1. An *ORTEP* diagram (Johnson, 1965) of 4-chloro-7-(iodoacetyl)amino-3-methoxyisocoumarin. Ellipsoids are plotted at the 50% probability level.

Experimental

The title compound was recrystallized from MeOH/H_2O solution.

Crystal data

$C_{12}H_9ClINO_4$
$M_r = 393.43$
Monoclinic
$P2_1/c$
$a = 12.165\ (9)$ Å
$b = 12.598\ (11)$ Å
$c = 8.962\ (5)$ Å
$\beta = 94.84\ (5)°$
$V = 1369\ (2)$ Å^3
$Z = 4$
$D_x = 1.910$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 15 reflections
$\theta = 6.25$–$12.07°$
$\mu = 2.52$ mm^{-1}
$T = 295$ K
Plate
0.53 × 0.26 × 0.03 mm
Yellow

Data collection

Syntex $P2_1$ diffractometer
ω scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.78$, $T_{max} = 1.00$
2580 measured reflections
2412 independent reflections
1398 observed reflections [$I > 2.5\sigma(I)$]
$R_{int} = 0.016$
$\theta_{max} = 25°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 10$
3 standard reflections monitored every 97 reflections
intensity decay: ±3.2%

Refinement

Refinement on F
$R = 0.050$
$wR = 0.052$
$S = 1.56$
1398 reflections
173 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0003F]$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.98$ e Å^{-3}
$\Delta\rho_{min} = -0.66$ e Å^{-3}
Extinction correction: none
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)*

$B_{eq} = (1/3)\Sigma_i\Sigma_j B_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
C(1)	0.8395 (8)	0.4222 (9)	0.5038 (11)	3.4 (5)
O(2)	0.7498 (5)	0.4228 (5)	0.3983 (7)	3.6 (3)
C(3)	0.7046 (8)	0.3319 (10)	0.3417 (11)	3.7 (5)
C(4)	0.7417 (8)	0.2358 (9)	0.3821 (12)	3.6 (5)
C(5)	0.8770 (8)	0.1305 (8)	0.5475 (11)	3.4 (5)
C(6)	0.9645 (8)	0.1293 (8)	0.6552 (11)	3.3 (5)
C(7)	1.0132 (7)	0.2224 (8)	0.7119 (10)	2.7 (4)
C(8)	0.9729 (7)	0.3191 (7)	0.6613 (10)	2.8 (4)
C(9)	0.8819 (7)	0.3205 (8)	0.5514 (11)	2.9 (4)
C(10)	0.8331 (7)	0.2272 (8)	0.4942 (10)	2.7 (4)
O(11)	0.8711 (6)	0.5085 (6)	0.5463 (8)	4.8 (4)
O(12)	0.6201 (6)	0.3486 (6)	0.2373 (8)	5.1 (4)
C(13)	0.5923 (9)	0.4562 (10)	0.1960 (14)	5.6 (6)
Cl(14)	0.67848 (22)	0.12479 (22)	0.3014 (3)	4.74 (13)
N(15)	1.1021 (6)	0.2112 (6)	0.8251 (8)	3.3 (4)
C(16)	1.1648 (8)	0.2904 (9)	0.8918 (11)	3.0 (5)
C(17)	1.2482 (7)	0.2515 (8)	1.0146 (11)	3.2 (5)
I(18)	1.40163 (6)	0.22135 (9)	0.92229 (10)	6.57 (5)
O(19)	1.1590 (6)	0.3831 (6)	0.8574 (9)	4.8 (4)

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

C(1)—O(2)	1.385 (9)	C(6)—C(7)	1.394 (12)
C(1)—O(2)	1.382 (11)	C(6)—C(7)	1.391 (14)
C(1)—C(9)	1.433 (15)	C(7)—C(8)	1.376 (14)
C(1)—O(11)	1.204 (14)	C(7)—N(15)	1.425 (11)
O(2)—C(3)	1.350 (14)	C(8)—C(9)	1.418 (13)
C(3)—C(4)	1.331 (17)	C(9)—C(10)	1.395 (14)
C(3)—O(12)	1.347 (12)	O(12)—C(13)	1.439 (15)
C(4)—C(10)	1.439 (13)	N(15)—C(16)	1.363 (13)
C(4)—Cl(14)	1.725 (11)	C(16)—C(17)	1.514 (14)
C(5)—C(6)	1.375 (14)	C(16)—O(19)	1.209 (14)
C(5)—C(10)	1.398 (14)	C(17)—I(18)	2.139 (9)
O(2)—C(1)—C(9)	116.9 (9)	C(8)—C(9)—C(10)	121.9 (9)
O(2)—C(1)—O(11)	115.1 (9)	C(4)—C(10)—C(5)	123.7 (9)
C(9)—C(1)—O(11)	128.0 (9)	C(4)—C(10)—C(9)	118.2 (9)
C(1)—O(2)—C(3)	121.7 (8)	C(5)—C(10)—C(9)	118.1 (8)
O(2)—C(3)—C(4)	123.4 (9)	C(3)—O(12)—C(13)	118.3 (9)
O(2)—C(3)—O(12)	113.1 (10)	C(3)—C(4)—Cl(14)	119.6 (8)
C(4)—C(3)—O(12)	123.5 (10)	C(10)—C(4)—Cl(14)	121.5 (8)
C(3)—C(4)—C(10)	118.9 (10)	C(6)—C(5)—C(10)	119.9 (9)
C(7)—N(15)—C(16)	127.0 (8)	C(17)—C(16)—O(19)	121.3 (9)
C(5)—C(6)—C(7)	121.9 (9)	C(16)—C(17)—I(18)	109.2 (6)
N(15)—C(16)—C(17)	113.5 (9)	C(8)—C(7)—N(15)	123.4 (9)
N(15)—C(16)—O(19)	125.2 (9)	C(7)—C(8)—C(9)	118.4 (8)
C(6)—C(7)—C(8)	119.8 (8)	C(1)—C(9)—C(8)	117.3 (9)
C(6)—C(7)—N(15)	116.8 (8)	C(1)—C(9)—C(10)	120.8 (9)

Software package used to solve the structure: *NRCVAX* (Gabe, Lee & Le Page, 1985)

We are grateful to the National Institutes of Health (grants HL34035 and HL29037) for financial support of this work.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: SZ1024). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 453–455

Dipyridiniomethane 1-Iodo-*closo*-decaborate, $[(C_5H_5N)_2CH_2][1\text{-}IB_{10}H_9]$

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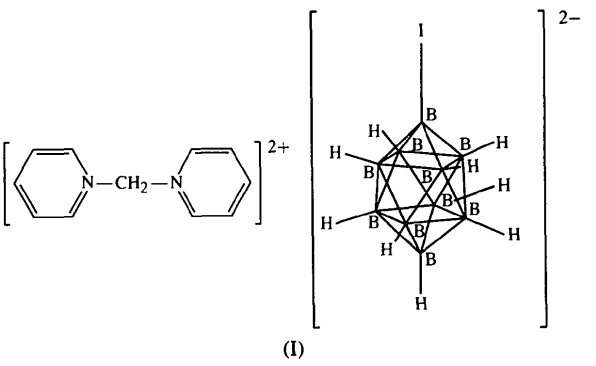
Abstract

The structure of the title compound [*N*,*N*′-methylenedipyridinium 1-iodononahydro-*closo*-decaborate(2−), $C_{11}H_{12}N_2^{2+}.B_{10}H_9I^{2-}$] has been determined by single-crystal X-ray diffraction at room temperature. This is the first halogeno derivative of *closo*-$[B_{10}H_{10}]^{2-}$ 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 $[1\text{-}IB_{10}H_9]^{2-}$ is significantly shorter than the distance of 2.230 (2) Å in the $[2\text{-}IB_{10}H_9]^{2-}$ isomer.

Comment

As part of our work on *closo*-borates we are interested in derivatives of $[B_{10}H_{10}]^{2-}$ and the sequence of substituting reactions. By treatment with chlorine, bromine and iodine, compounds of the type *closo*-$[2\text{-}XB_{10}H_9]^{2-}$ (X = Cl, Br, I) are formed, which have been characterized by ^{11}B and $^{11}B(^1H)$ NMR, and vibrational spectroscopy (Preetz, Srebny & Marsmann, 1984) as well as by X-ray studies (Preetz & Nachtigal, 1995). After iodination, the isomeric species $[1\text{-}IB_{10}H_9]^{2-}$, substituted in an apical position of the B_{10} cage, could be isolated from the reaction mixture in minor yield. Using the dipyridiniomethane dication (Brüdgam & Hartl, 1986), the *AB*-type salt $[(C_5H_5N)_2CH_2][1\text{-}IB_{10}H_9]$, (I), was precipitated from aqueous solution as single crystals.



(I)

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 $[1\text{-}IB_{10}H_9]^{2-}$ 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 $[B_6H_6I]^-$ [2.174 (3) Å; Preetz & Sonnak, 1994] and $[B_6I_6]^{2-}$ (2.18 Å; Heinrich, Keller & Preetz, 1990). The B—I distance is significantly lengthened if the *ipso*-B atom is connected to five other B atoms as in $[2\text{-}IB_{10}H_9]^{2-}$ [2.230 (2) Å; Preetz & Nachtigal, 1995] and $[IB_{12}H_{11}]^{2-}$ [2.226 (4) Å; Haeckel & Preetz, 1995].

The $[(C_5H_5N)_2CH_2]^{2+}$ 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 &

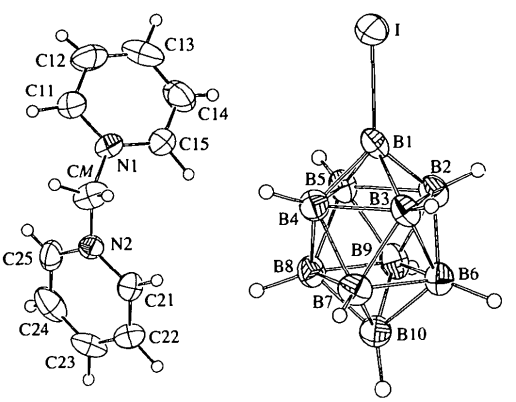


Fig. 1. View of the $[(C_5H_5N)_2CH_2]^{2+}$ cation and $[1\text{-}IB_{10}H_9]^{2-}$ anion. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms; H atoms are drawn as spheres of arbitrary radii.