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Bis{1a,8b-dihydro(1,1-$^2H_2$)-2*H*-benzo[*a*]cyclopropa[*c*]cyclohepten-2-one}hydrogen(I) Hexachloroantimonate, $[H(C_{12}H_8D_2O)_2][SbCl_6]$

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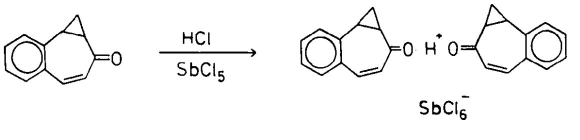
Abstract. $M_r = 675{\cdot}9$, monoclinic, space group $I2/c$, $a = 18{\cdot}336$ (3), $b = 8{\cdot}056$ (2), $c = 17{\cdot}982$ (3) Å, $\beta = 99{\cdot}56$ (2)°, $V = 2619$ (1) Å^3, $Z = 4$, $D_x = 1{\cdot}714$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 16{\cdot}94$ cm^{-1}, $T = 238$ K, $F(000) = 1336$, $R = 0{\cdot}059$ for 2714 unique observed reflections. The cation consists of two ketones bridged by the proton giving a very strong hydrogen bond [O···O 2·44 (1) Å]. The hemi-protonation has not caused extensive delocalization of the olefinic bond [1·341 (8) Å] nor changed the bonds, especially the bridging bond [1·544 (8) Å] in the cyclopropane group significantly. The side bond in the cyclopropane group [1·515 (9) Å] nearest the ketone group is longer than the other side bond [1·471 (9) Å], consistent with some conjugation with the hemi-protonated ketone group.

Introduction. Carbenium ions are important intermediates in many organic reactions and as such they have been the subject of much experimental and theoretical study. In recent years with the development of super-acid solvents, it has been possible to generate these ions as long-lived species. Despite this, relatively few structural studies have been reported (Sundaralingam & Chwang, 1976).

We have recently reported the structure of the 2-hydroxyhomotropylium cation and provided conclusive evidence that homoaromatic delocalization was present (Childs, Varadarajan, Lock, Faggiani, Fyfe & Wasylishen, 1982). It was not possible to obtain very accurate bond lengths for the whole cation because of disorder. For this reason and to probe further the structural consequences of homoaromaticity, we attempted to prepare the corresponding benzannelated cation where C(5), C(6) is made part of a benzene ring (I). The desired cation was not obtained, however, and instead a hemi-protonated species with one proton bridging two ketones was produced.



Experimental. The material was prepared by the protonation of la,8b-dihydro(1,1-$^2H_2$)-2*H*-benzo[*a*]cyclopropa[*c*]cyclohepten-2-one in strong acid. Preparation took place in an evacuated, flame-dried reaction vessel, the whole being handled in a nitrogen atmosphere in a glove bag. A solution of $SbCl_5$ (0·58 g) in CH_3NO_2 (2 ml) was introduced into the vessel, cooled to 258 K, and the solution saturated with HCl by means of a vacuum line. Dry nitrogen was then admitted to the vessel and a cold (258 K) solution of an equimolar portion of the ketone (0·335 g) in CH_2Cl_2 (2 ml) was added. The mixture was stirred for about 25 min and dry benzene (100 ml) was added slowly when the product precipitated as a greenish-yellow mass. The product was separated by filtration, and washed with benzene. Crystals, suitable for the X-ray study, were obtained by slow crystallization of the product from a CH_2Cl_2 solution at 253 K.

Density not measured owing to instability of product at room temperature and in air. Crystal used: needle, $l = 0{\cdot}25$ mm, roughly square cross-section, 0·175 mm on a side. Syntex $P2_1$ diffractometer, Mo radiation, 15 reflections $20{\cdot}3° < 2\theta < 24{\cdot}9°$ for cell measurement. Systematic absences: hkl $h + k + l = 2n + 1$, $h0l$ $h, l = 2n + 1$.* No absorption correction applied, max. error in F 3%, $h,k,\pm l$ quadrant collected, $(2\theta)_{\max} = 45°$; standards (e.s.d.): $4\bar{1}\bar{3}$ (0·015), $40\bar{4}$ (0·012); of 3011 non-equivalent reflections measured, 2714 were 'observed' with $I > 0$, 297 unobserved. Sb from Patterson map, other non-hydrogen atoms from electron density difference map; full-matrix least-squares refinement minimized $\sum w(|F_o| - |F_c|)^2$. H atoms from difference map, their positional parameters refined for one cycle to give rough errors but not varied further. Parameters refined: scale, secondary extinction, x,y,z, U_{ij}, except x,y,z for D, total 152 variables; $wR = 0{\cdot}0547$, S

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* The non-standard setting, $I2/c$, of $C2/c$ can be transformed to the standard cell $a = 23{\cdot}453$ (4), $b = 8{\cdot}056$ (2), $c = 17{\cdot}982$ (3) Å and $\beta = 129{\cdot}56$ (2)° by the matrix $(\bar{1}0\bar{1}/0\bar{1}0/001)$; equivalent positions of the non-standard space group are x,y,z; $-x,-y,-z$; $-x,y,\frac{1}{2}-z$; $x,-y,\frac{1}{2}+z$; $\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z$; $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$; $\frac{1}{2}-x, \frac{1}{2}+y, -z$; $\frac{1}{2}+x, \frac{1}{2}-y, z$. It was chosen to avoid the use of a very obtuse β angle of more than 120°.

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$= 0{\cdot}90$, $w = (\sigma^2 + 0{\cdot}00075\,F_o^2)^{-1}$; max. shift/error 0·006, ave. 0·0018; final $\Delta\rho$ peaks: max. 0·59, min. 0·66 e Å^{-3}; secondary-extinction parameter = 0·00013; scattering factors and anomalous-dispersion corrections (Sb, Cl) from *International Tables for X-ray Crystallography* (1974). Initial data treatment – *XRAY76* (Stewart, 1976), structure solution – *SHELX* (Sheldrick, 1976), planes, dihedral angles – *NRC22* (Pippy & Ahmed, 1978), diagrams – *ORTEP*II (Johnson, 1976).

Discussion. Atomic coordinates are given in Table 1 and bond lengths and angles in Table 2.* The most noticeable feature of the structure of the cation (Fig. 1) is the very strong hydrogen bond binding the two ketones together [O···O′ 2·44 (1) Å]. Similar very strong hydrogen bonds have been observed between two CO groups in bis(acetamide)hydrogen(I) chloride [O···O′ 2·451 (1) Å] (Muir & Speakman, 1979) and its bromide [O···O′ 2·438 (5) Å] (Groth, 1977). The distance is almost short enough to suggest a symmetric hydrogen bond. The geometry [C—O···O′ 115·9 (7)°, dihedral angle C(1)C(2)C(3)O – C(2)O···O′ 5·4 (7)°] is consistent with an sp^2-bonded O atom and there is an inversion centre at the middle of O···O′. Nevertheless we were unable to find the bridging H atom, even though all others were located.

Three types of hydrogen bonds have been identified for apparently symmetric molecules with hydrogen bonds (Hamilton & Ibers, 1968; Vinogradov & Linnell, 1971). These are a symmetric hydrogen bond, described by a single potential minimum, an asymmetric hydrogen bond described by a double potential minimum with a relatively high barrier and a hydrogen bond described by a potential with a double minimum with a very low barrier such that the ground vibrational level lies near the top of the potential barrier. In symmetric systems it has proved possible to locate the H atom (Hamilton & Ibers, 1968) and we have generally managed to locate the H atoms in asymmetric hydrogen bonds (Britten, Lippert, Lock & Pilon, 1982; Howard-Lock, Lock & Smalley, 1983) where there is, apparently, a high barrier. The failure to locate the bridging H atom suggests that it has a very poorly defined position corresponding to the double minimum potential with a very low barrier.

Bond lengths within the molecule differ significantly from those obtained for the 2-hydroxyhomotropylium cation described previously (Childs *et al.*, 1982) and suggest that hemi-protonation has not changed the

Table 1. *Atomic positional parameters* (×10^4) *and temperature factors* (Å^2 ×10^3)

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta).$$

	x	y	z	U_{eq}
Sb	0	8774 (1)	2500	30·0
Cl(1)	206 (1)	8777 (2)	1232 (1)	48·0
Cl(2)	1297 (1)	8724 (2)	2936 (1)	45·7
Cl(3)	0	5824 (2)	2500	45·8
Cl(4)	0	1695 (2)	2500	50·4
C(1)	1236 (3)	7371 (7)	5868 (4)	61
C(2)	1719 (3)	6825 (9)	6538 (4)	61
C(3)	1792 (3)	5141 (9)	6780 (3)	53
C(4)	1748 (3)	3762 (8)	6357 (3)	46
C(5)	1640 (2)	3504 (6)	5550 (3)	35
C(6)	1383 (3)	4707 (7)	4997 (3)	38
C(7)	1055 (3)	6337 (7)	5138 (3)	50
C(8)	500 (4)	6506 (9)	5637 (4)	58
C(9)	1850 (3)	1939 (7)	5319 (4)	52
C(10)	1798 (3)	1553 (9)	4566 (4)	64
C(11)	1575 (3)	2707 (10)	4032 (4)	63
C(12)	1370 (3)	4295 (9)	4242 (3)	52
O	2066 (3)	7973 (7)	6954 (3)	94

Table 2. *Selected interatomic distances* (Å) *and angles* (°)

C(1)—C(2)	1·439 (10)	C(2)—C(3)	1·425 (10)
C(3)—C(4)	1·341 (8)	C(4)—C(5)	1·446 (7)
C(5)—C(6)	1·413 (7)	C(6)—C(7)	1·484 (7)
C(7)—C(8)	1·471 (9)	C(8)—C(1)	1·515 (9)
C(1)—C(7)	1·544 (8)	C(2)—O	1·289 (6)
C(5)—C(9)	1·402 (7)	C(9)—C(10)	1·376 (9)
C(10)—C(11)	1·350 (10)	C(11)—C(12)	1·403 (9)
C(12)—C(6)	1·393 (7)	O—O′	2·435 (12)
Sb—Cl(1)	2·372 (1)	Sb—Cl(2)	2·377 (1)
Sb—Cl(3)	2·376 (2)	Sb—Cl(4)	2·353 (2)
C(8)—C(1)—C(2)	119·0 (6)	C(7)—C(1)—C(2)	124·2 (5)
C(1)—C(2)—C(3)	124·1 (5)	C(2)—C(3)—C(4)	128·5 (5)
C(3)—C(4)—C(5)	132·3 (5)	C(4)—C(5)—C(6)	125·6 (5)
C(5)—C(6)—C(7)	125·7 (5)	C(6)—C(7)—C(1)	125·9 (5)
C(6)—C(7)—C(8)	121·8 (5)	C(8)—C(1)—C(7)	57·5 (4)
C(1)—C(7)—C(8)	60·2 (4)	C(7)—C(8)—C(1)	62·3 (4)
C(1)—C(2)—O	116·2 (7)	C(3)—C(2)—O	119·5 (7)
C(4)—C(5)—C(9)	115·4 (5)	C(6)—C(5)—C(9)	118·9 (5)
C(5)—C(9)—C(10)	121·1 (6)	C(9)—C(10)—C(11)	120·5 (6)
C(10)—C(11)—C(12)	120·0 (5)	C(11)—C(12)—C(6)	121·1 (6)
C(12)—C(6)—C(5)	118·2 (5)	C(12)—C(6)—C(7)	115·8 (5)
Cl(1)—Sb—Cl(2)	90·4 (1)	Cl(1)—Sb—Cl(3)	90·1 (1)
Cl(1)—Sb—Cl(4)	89·9 (1)	Cl(2)—Sb—Cl(3)	89·0 (1)
Cl(2)—Sb—Cl(4)	91·0 (1)	Cl(3)—Sb—Cl(4)	180·0 (1)

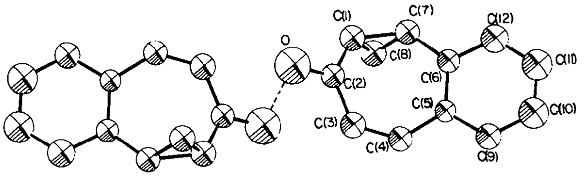

Fig. 1. The cation $[H(C_{12}H_8D_2O)_2]^+$. The dotted line indicates the O—H—O hydrogen bond.

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* Anisotropic temperature factors, H-atom coordinates, bond distances and angles, best planes, dihedral and torsional angles and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39276 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

structure for most of the molecule from that expected for the neutral ketone. Thus the short C(3)—C(4) bond [1·341 (8) Å] suggests that the double bond has not been extensively delocalized. Further the C—C distances in the cyclopropane group have not changed significantly from other similar neutral molecules (Dusausoy, Hanquet & Guilard, 1981; Contreras, MacLean, Faggiani & Lock, 1981). In particular there is no significant lengthening of the C(1)—C(7) bond [1·544 (8) Å *vs* range 1·513 (11)–1·555 (7), ave. 1·535 (10) Å] such as was observed for the 2-hydroxyhomotropyllium ion [1·626 (8) Å] (Childs *et al.*, 1982). The other two sides of the cyclopropane group differ significantly [by $3{\cdot}3\sigma$ where $\sigma = (\sigma_1^2 + \sigma_2^2)^{1/2}$] with the C(1)—C(8) bond which is nearer the ketone being longer. While the errors preclude certainty, a similar effect has been suggested in three systems previously studied (Dusausoy *et al.*, 1981) where the C—C bond nearer the ketone consistently has a higher mean length [range 1·499 (11)–1·530 (11), ave. 1·516 (10) Å] than the other C—C bond [range 1·477 (11)–1·509 (10) ave. 1·496 (10) Å]. This inequality in the bond distances of a cyclopropane adjacent to a carbonyl is consistent with what would be expected for a conjugation interaction between the ring and the carbonyl group and would be amplified on protonation or hemi-protonation, as is observed.

The C(2)—O bond is significantly longer than in the neutral molecules [1·289 (6) *vs* range 1·191 (9)–1·222 (4), ave. 1·206 (9) Å] (Dusausoy *et al.*, 1981; Contreras *et al.*, 1981). This is presumably caused by the very stong hydrogen bond between the carbonyl groups. Similar lengthening of the CO bond was observed in the bis(acetamide)hydrogen(I) cation (Muir & Speakman, 1979; Groth, 1977; Kitano & Kuchitsu, 1973; Denne & Small, 1971) and in protonated acetic acid salts (Jönsson & Olovsson, 1968; Kvick, Jönsson & Olovsson, 1969).

Consideration of the various planes in the molecule shows some distortion, compared to the 2-hydroxyhomotropylium cation. The benzene ring is essentially planar but the steric restrictions of this ring mean that C(2), C(3), C(5) and C(6) are not coplanar. The C(2)—C(3) bond is twisted relative to C(5)—C(6) such that the atoms are between 0·044 (4) to 0·075 (6) Å out of the best plane. The distortion is less for the C(1), C(2), C(6) and C(7) plane, the maximum deviation being 0·019 (6) Å. Despite these distortions the dihedral angles between planes are very similar to those observed for the 2-hydroxyhomotropylium ion (Childs *et al.* 1982), corresponding angles being *A*[C(4)C(3)C(5)]–*B*[C(2)C(3)C(5)C(6)] 171 (1) *vs* 172 (1)°, *B*–*C*[C(1)C(2)C(6)C(3)] 155 (1) *vs* 150 (1)° and *C*–*D*[C(1)C(7)C(8)] 108 (1) *vs* 112 (1)°.

The packing (Fig. 2) consists of layers of cations with the backbone oriented roughly along the (220) planes. Projections from these cations give cation–cation contacts in layers at $z = 0,\frac{1}{2}$. The result is a series of channels along **b** at $x = \frac{1}{4},\frac{3}{4}$, $z = 0,\frac{1}{2}$, in which the $SbCl_6^-$ ions are stacked. There is no evidence of any strong interactions which might distort the structure of the cation.

In conclusion, the formation of such a hemi-protonated system was unexpected. The ratios of reagents used was such that a molar excess of acid was present during the preparation of the salt and variation in the ratios did not change the nature of the material obtained in the solid state. Dissolution of the crystallized hemi-protonated salt in CD_2Cl_2 gave, however, a ^1H NMR spectrum which was in between that of the fully protonated material and the starting ketone. Solubility problems limited taking the spectra at very low temperatures; however, as far as we could go (193 K) only one set of averaged signals could be seen. This suggests that either the hemi-protonated structure is maintained in solution or that exchange between fully protonated and neutral ketone must be still fast at this temperature on the NMR time scale.

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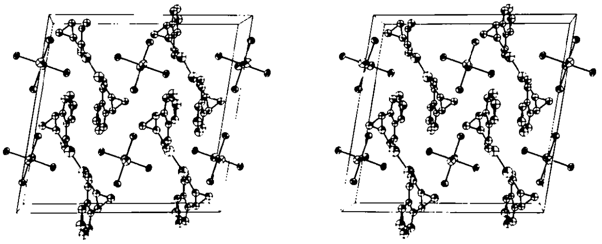

Fig. 2. The packing of $[H(C_{12}H_8D_2O)_2][SbCl_6]$. **a** and **c*** are parallel to the bottom and sides of the page, respectively, and the view is down **b**.

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1-(*p*-Chlorophenyl)biguanide Hydrochloride, $C_8H_{11}ClN_5^+.Cl^-$

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Abstract. $M_r = 248{\cdot}1$, monoclinic, $P2_1/n$, $a = 13{\cdot}604\,(7)$, $b = 5{\cdot}719\,(5)$, $c = 15{\cdot}376\,(8)$ Å, $\beta = 108{\cdot}26\,(4)°$, $V = 1136{\cdot}03$ Å^3, $Z = 4$, $D_m = 1{\cdot}433\,(5)$, $D_x = 1{\cdot}450$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}55$ mm^{-1}, $F(000) = 512$, room temperature, $R = 0{\cdot}046$ for 1843 observed reflexions $[I > \sigma(I)]$. The Cl^- ion is coordinated octahedrally to six N atoms at a mean distance of 3·272 (2) Å. The C—N bonds of the biguanide moiety are within the range 1·307 (3)–1·352 (3) Å; it consists of two planes at an angle of 50·72 (5)° to each other.

Introduction. The title compound is one of a series of substances well known for their pharmacological activity. Crystal data for a variant unit cell of this and for a number of related compounds have already been published (Brown, 1967). This structure determination was carried out to confirm the configuration of the biguanide residue.

Experimental. Acicular crystals (1·0 × 0·5 × 0·2 mm) prepared by Dr J. A. Hendry, Imperial Chemical Industries Limited (Pharmaceuticals Division). Lattice parameters obtained initially from rotation and Weissenberg photographs and refined by least-squares fit to 26 reflexions on the diffractometer. D_m by flotation in NaI solution. Nonius CAD-4 diffractometer. Two standard reflexions, no variation in intensity. $\theta_{\max} = 25°$ (Mo $K\alpha$ radiation). Index range h 0 to 16, k 0 to 6, l −18 to +17. Corrections for Lp effects but not for absorption or extinction. Structure solved by direct methods with *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by least squares on F with $\sqrt{w} = 1/F_o$ using programs of Ahmed, Hall, Pippy & Huber (1970) implemented on our DEC-10 computer. $B_{\rm iso}$ used initially and B_{ij} finally. Approximate H-atom coordinates from difference Fourier maps; included in structure factor calculations without refining at idealized positions with $B_{\rm iso} = 5{\cdot}0$ Å^2 for phenyl H and 6·0 Å^2 for biguanide H. 153 reflexions $[I < \sigma(I)]$ discarded. Δ/σ during last refinement cycle <0·2. Max. $\Delta\rho$ in final difference map $\pm 0{\cdot}2$ e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974). $R = 0{\cdot}046$, $R_w = 0{\cdot}127$ for the 1843 observed reflexions.

Discussion. The atomic coordinates and equivalent isotropic temperature factors are given in Table 1,* and bond lengths and angles in Table 2. The atom numbering and molecular geometry are shown in Fig. 1.

The Cl^- ion is coordinated in the form of a severely distorted octahedron to six N atoms at distances shown in Fig. 1 [mean Cl^- to N = 3·272 (2) Å, compared with 3·270 Å in the 5-isopropyl derivative (Brown, 1967)]. There is some uncertainty as to whether these are hydrogen bonds or not; suffice it to say that there is an

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* Lists of structure factors, anisotropic thermal parameters, calculated H-atom parameters, least-squares-planes calculations and intermolecular distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39387 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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