Molecular Structure of 10-Bromo-9-triptycyl Iodoformate: a Molecule with a Unique Functional Group

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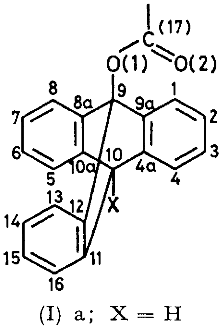
9-Triptycyl iodoformate (Ia), unique in containing a stable iodoformyl substituent, was subjected to *X*-ray crystallographic study to determine whether the conformation throws light on its unexpected stability. Although attempts to solve the structure were unsuccessful, that of the 10-bromo-derivative (Ib) was determined. Crystals are orthorhombic, a = 30.550(5), b = 8.255(5), c = 14.040(5), space group *Pbca*, Z = 8. This structure was solved by Patterson and difference-Fourier methods, and refined by the method of least squares to R 0.105 for 941 reflections. The molecule is characterised by an unusually short C–1 bond length of 1.98(3) Å and a large number of crowded intramolecular contacts, particularly between the carbonyl oxygen and neighbouring aromatic carbon and hydrogen atoms. These features are discussed in relation to the stability of the iodoformyl group.

STUDIES on the irradiative decomposition of half-esters of oxalic acid in the presence of mercury(II) oxide and iodine led to a method for the substitution of bridgehead alcohols in apocamphan-1-ol by iodine[1] and bromine.[2] By extending this study[3] to other systems it was found that 9-triptycyl hydrogen oxalate decomposed under these irradiative conditions to 9-triptycyl iodoformate (Ia), which was the first iodoformate to be characterised beyond doubt.[4] An *X*-ray crystallographic study was therefore undertaken to determine whether there were structural features in the molecule which could be related to the unexpected stability of the iodoformyl group in this environment. Although attempts to solve the structure were not successful, the structure of the 10-bromo-derivative (Ib) was established.



(I) a; X = H
b; X = Br

EXPERIMENTAL

10-Bromo-9-triptycyl Iodoformate.—The oxalate half ester of 9-hydroxy-10-bromotriptycene, treated as in ref. 3 gave *10-bromo-9-triptycyl iodoformate*, m.p. 240 °C, $\nu_{max.}$ ($CHCl_3$) 1 795, 1 460, 1 300, 1 185, 1 100, 960, 895, and 730 cm^{-1}; δ($CDCl_3$) 6.95—7.9 (m).

Crystal Data.—(*a*) *9-Triptycyl iodoformate*. $C_{21}H_{13}O_2I$, M = 424.2, Orthorhombic, a = 21.83(1), b = 9.04(1), c = 8.67(1) Å, U = 1 711.1 $Å^3$, D_c = 1.646 g cm^{-3}, Z = 4.

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Space group P$na2_1$ (No. 33, C^9_{2v}). Mo-K_α radiation, $\lambda = 0.710\,7$ Å; μ(Mo-K_α) = 19.06 cm^{-1}. (*b*) *10-Bromo-9-triptycyl iodoformate*. $C_{21}H_{12}O_2BrI$, $M = 503.1$, $a = 30.550(5)$, $b = 8.255(5)$, $c = 14.040(5)$ Å, $U = 3\,540.8$ Å^3, $D_c = 1.887$ g cm^{-3}, $Z = 8$. Space group P*bca* (No. 61, $V_h{}^{15}$). μ(Mo-K_α) = 38.95 cm^{-1}.

Intensity Measurements.—Three-dimensional *X*-ray diffraction data from a small single crystal of 10-bromo-9-triptycyl iodoformate [0.250(5) × 0.140(5) × 0.025(5) mm] were collected on a Philips computer-controlled four-circle diffractometer by use of graphite-monochromated Mo-K_α radiation. Since the compound is sensitive to *X*-rays (very much so for Cu-K_α, less for Mo-K_α), intensities were obtained by a rapid-scan ω—2θ technique. Peaks were scanned for 30 s, and no background counts were made; these were estimated by interpolation from counts made at the angular setting of systematically absent reflections. Frequent monitoring over three standard reflections confirmed that no appreciable decomposition had taken place during the 18 h of data collection. In the range θ 4—24° 1 131 maxima of a possible 1 936 in an octant of reciprocal space (*h, k, l*) and having $I \geqslant 1.65\ \sigma(I)$ were considered observed. Besides the usual corrections for Lorentz and polarisation effects, absorption corrections were made according to the method of Busing and Levy,[5] with program ABSCOR,[6] by use of a sampling grid of 512 points within the crystal. Absorption coefficients varied in the range 1.19—1.719. No corrections were made for extinction.

Structure Solution and Refinement.—The first attempt at structural analysis was on 9-triptycyl iodoformate, using 1 200 intensities collected on a four-circle diffractometer. Although a Patterson synthesis yielded the iodine co-ordinates and allowed identification of the space group, further attempts at solving the structure by difference-Fourier methods were unsuccessful; the standard procedure of resolving the pseudo-centrosymmetry generated by a single heavy atom in polar space groups was not effective, and no molecular fragment could be recognised from the confusion of mirrored peaks. However, no problems were experienced in solving the structure of the 10-bromo-derivative. Co-ordinates for both heavy atoms were derived from a sharpened Patterson synthesis, and the remaining non-hydrogen atoms in the asymmetric unit (one molecule) were located in two subsequent difference syntheses. The quality of the intensity data was not regarded as being good enough to justify anisotropic refinement of all atoms (non-positive-definite temperature matrices tended to occur). The aromatic ring carbons, with four hydrogens added artificially to each ring, were therefore constrained to refine as rigid C_6H_4 units with idealised benzenoid geometry. Carbon atoms were assigned individual isotropic temperature factors, and hydrogen atoms a common isotropic temperature factor. Four cycles of full-matrix least-squares refinement, with the final two cycles limited to 941 structure factors with $\theta < 17.5°$, gave convergence to a final *R* of 0.105. The function $\Sigma(||F_o| - |F_c||)^2$ (unit weights) was minimised. In order to check whether appreciable dissociation at the C–I bond occurred during irradiation (the crystal was deep yellow afterwards), the site-occupation factor of the iodine atom was allowed to vary in the final refinement. Its final value [0.99(2)] did not indicate significant deviation from unity. Atomic scattering factors were calculated analytically,[7] those of iodine and bromine being corrected for anomalous dispersion effects.[8] The program SHELX [9] was used for structure solution and refinement. Positional and thermal parameters are listed in Table 1, and bond lengths and angles, excluding those for the aromatic rings (which were constrained to C–C 1.395, C–H 1.080 Å; C–C–C 120°), in Table 2. In Table 3 data relevant to the best mean atomic planes are reported for the iodoformyl group and the aromatic rings. Observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 22113 (7 pp., 1 microfiche).*

TABLE 1

Fractional co-ordinates (× 10^4) and isotropic thermal motion parameters (Å^2 × 10^3) derived from least-squares refinement, with estimated standard deviations in parentheses

	x	*y*	*z*	U_{iso}
I	4 722(1)	1 066(4)	3 602(2)	†
Br	2 894(1)	1 013(5)	−1 097(3)	†
O(1)	4 265(6)	692(24)	1 947(14)	36(6)
O(2)	3 894(8)	1 939(29)	3 058(17)	60(7)
C(1)	3 984(5)	3 951(27)	1 261(12)	44(9)
C(2)	3 851(5)	5 466(27)	901(12)	44(10)
C(3)	3 523(5)	5 519(27)	211(12)	67(13)
C(4)	3 329(5)	4 097(27)	−119(12)	20(8)
C(4a)	3 462(5)	2 601(27)	241(12)	34(9)
C(5)	3 829(6)	−647(25)	−1 253(12)	47(10)
C(6)	4 229(6)	−1 411(25)	−1 412(12)	54(10)
C(7)	4 546(6)	−1 435(25)	−696(12)	44(10)
C(8)	4 462(6)	−696(25)	178(12)	33(9)
C(8a)	4 061(6)	68(25)	337(12)	32(9)
C(9)	3 894(10)	831(38)	1 263(21)	30(9)
C(9a)	3 790(5)	2 528(27)	931(12)	22(8)
C(10)	3 350(9)	958(35)	−115(19)	21(8)
C(10a)	3 744(6)	92(25)	−379(12)	21(8)
C(11)	3 168(6)	38(25)	787(12)	38(9)
C(12)	3 490(6)	−47(25)	1 490(12)	19(8)
C(13)	3 415(6)	−941(25)	2 317(12)	33(9)
C(14)	3 018(6)	−1 750(25)	2 442(12)	51(11)
C(15)	2 696(6)	−1 664(25)	1 739(12)	55(11)
C(16)	2 771(6)	−770(25)	912(12)	42(10)
C(17)	4 241(11)	1 367(42)	2 805(24)	45(10)
H(1)	4 238(5)	3 895(27)	1 796(12)	*
H(2)	4 001(5)	6 542(27)	1 157(12)	*
H(3)	3 419(5)	6 667(27)	−67(12)	*
H(4)	3 075(5)	4 153(27)	−653(12)	*
H(5)	3 584(6)	−628(25)	−1 808(12)	*
H(6)	4 295(6)	−1 983(25)	−2 089(12)	*
H(7)	4 856(6)	−2 027(25)	−819(12)	*
H(8)	4 707(6)	−715(25)	733(12)	*
H(13)	3 664(6)	−1 008(25)	2 861(12)	*
H(14)	2 960(6)	−2 442(25)	3 082(12)	*
H(15)	2 389(6)	−2 291(25)	1 835(12)	*
H(16)	2 522(6)	−704(25)	368(12)	*

* All atoms have $U_{iso} = 77(30)$. † Anisotropic thermal parameters in the form $T = \exp[-2\pi^2 \sum_i \sum_j a_i{}^* a_j{}^* h_i h_j U_{ij}]$ with parameters:

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I	96(3)	94(3)	46(2)	−1(2)	−34(2)	−21(2)
Br	63(3)	81(4)	39(3)	3(2)	−18(2)	9(3)

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* See Notice to Authors No. 7, in *J.C.S. Perkin II*, 1977, Index issue.

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TABLE 2

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances

I–C(17)	1.98(3)	C(9)–C(9a)	1.51(4)
Br–C(10)	1.97(3)	C(9)–C(12)	1.47(4)
C(17)–O(2)	1.22(4)	C(10)–C(10a)	1.46(4)
C(17)–O(1)	1.32(4)	C(10)–C(4a)	1.47(4)
C(9)–O(1)	1.49(4)	C(10)–C(11)	1.58(4)
C(9)–C(8a)	1.53(4)		

(*b*) Angles

I–C(17)–O(2)	126(3)	C(9)–C(9a)–C(4a)	114(1)
I–C(17)–O(1)	115(3)	C(9)–C(12)–C(11)	115(1)
C(17)–O(1)–C(9)	121(3)	Br–C(10)–C(4a)	113(2)
O(1)–C(17)–O(2)	119(3)	Br–C(10)–C(10a)	115(2)
O(1)–C(9)–C(8a)	105(2)	Br–C(10)–C(11)	108(2)
O(1)–C(9)–C(9a)	116(2)	C(10a)–C(10)–C(4a)	111(2)
O(1)–C(9)–C(12)	117(2)	C(10a)–C(10)–C(11)	104(2)
C(8a)–C(9)–C(9a)	101(2)	C(4a)–C(10)–C(11)	105(2)
C(8a)–C(9)–C(12)	105(2)	C(10)–C(4a)–C(4)	128(1)
C(9a)–C(9)–C(12)	111(2)	C(10)–C(10a)–C(5)	126(1)
C(9)–C(8a)–C(8)	128(1)	C(10)–C(11)–C(16)	130(1)
C(9)–C(9a)–C(1)	126(1)	C(10)–C(10a)–C(8a)	114(1)
C(9)–C(12)–C(13)	126(1)	C(10)–C(4a)–C(9a)	111(1)
C(9)–C(8a)–C(10a)	112(1)	C(10)–C(11)–C(12)	110(1)

(*c*) Non-bonded intramolecular distances (see Figure 2)

O(2) · · · H(8)	2.56	Br · · · H(5)	2.74
O(2) · · · H(1)	2.62	Br · · · H(4)	2.72
O(2) · · · C(8)	3.02	Br · · · H(16)	2.69
O(2) · · · C(1)	2.99	Br · · · C(5)	3.20
O(2) · · · C(8a)	3.05	Br · · · C(4)	3.18
O(2) · · · C(9a)	3.02	Br · · · C(16)	3.18
O(2) · · · C(9)	2.67	Br · · · C(10a)	2.89
C(9) · · · C(10)	2.55	Br · · · C(4a)	2.90
		Br · · · C(11)	2.55

TABLE 3

Data for various best mean atomic planes (shown in Fig. 3a)

(*a*) Equations *

Plane (A): $0.6916X - 0.0656Y - 0.7193Z = 6.9315$
Plane (B): $0.3827X - 0.8118Y - 0.4410Z = 3.1948$
Plane (C): $0.3737X + 0.8614Y - 0.3440Z = 4.5153$
Plane (D): $0.3602X + 0.8797Y - 0.3105Z = 4.3904$

(*b*) Atomic displacements † (Å)

Plane (D): I 0.0642, C(17) 0.039, O(1) −0.048, O(2) −0.028, C(9) −0.052, C(10) 0.056, Br 0.008

(*c*) Interplanar angles (°): (A)–(B) 129.4, (A)–(C) 116.7, (B)–(C) 113.9, (D)–(C) 2.3

* In orthogonal (Å) co-ordinates; the coefficient on the right-hand side represents the distance of the plane from the origin. † All atoms included in the derivation of plane (D). Displacements are not recorded for aromatic planes (A)–(C), since these atoms lie exactly on the planes.

RESULTS

Description of the Structure.—A perspective view of the 10-bromo-9-triptycyl iodoformate molecule is given in Figure 1; the numbering of the hydrogen atoms, which are omitted, follows that of the carbon atoms to which they are bonded. As was expected, the iodoformyl atoms only deviate slightly from a plane which is approximately coplanar with aromatic ring C (Table 3). The iodine atom is *trans* with respect to bridgehead atom C(9), its distance from C(17) [1.98(3) Å] being exceptionally short for a C–I bond.

The molecule is characterised by a large number of intramolecular nonbonded contacts which are of the order of or less than the sum of the appropriate van der Waals radii,[10] (Figure 2 and Table 2). These show, firstly, that the bromine atom is in a rather crowded environment and secondly, that the iodoformyl group has hardly any torsional freedom around the O(1)–C(9) bond. The C–Br bond length [1.97(3) Å] confirms the value [1.97(1) Å] found for 9-bromotriptycene.[11]

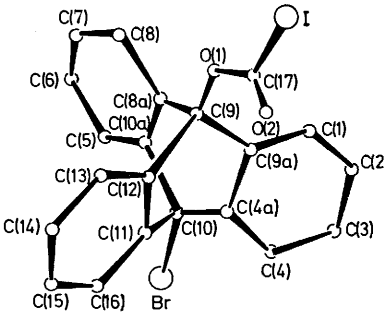

FIGURE 1 Perspective view of the 10-bromo-9-triptycyl iodoformate molecule, excluding hydrogen atoms

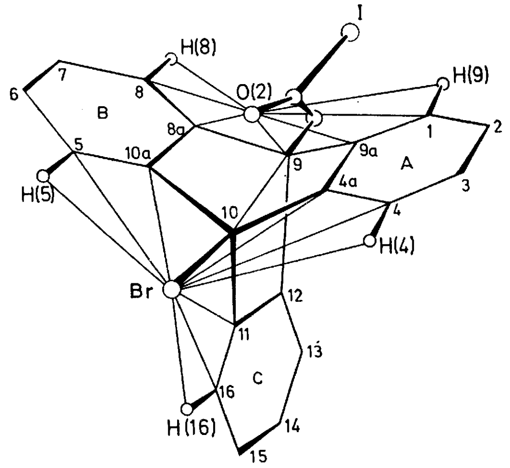

FIGURE 2 Non-bonded intramolecular contact distances (see also Table 2)

The triptycene carbon skeleton does not possess the three-fold rotational symmetry of the parent molecule, the angles between the ring planes deviating from 120° by 3—10° (Table 3). Of the three other triptycene derivatives with known structure,[11-13] that of 9-β-chloroethyltriptycene[13] displays the same distortion (Figure 3, Table 4). These two molecules are characterised by a similar conformation of the bridgehead substituents: in both cases the environment of the second atom from the bridgehead is such that crowded contacts are made with the adjacent ring atoms (by the carbonyl oxygen atom and the β-methylene hydrogen atoms in the iodoformyl- and chloroethyl-derivatives, respectively), thus forcing the angle μ_1 to open out by 10°. Further evidence for overcrowding in the chloroethyl-derivative

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is afforded (i) by the strain at the α-position, where the C–C–C tetrahedral angle is increased to 114.7°, and (ii) by the *ca.* 2.0 Å distances of the β-methylene hydrogen atoms to their nearest aromatic counterparts. The inequality in the remaining two angles, μ_2 and μ_3, which occurs in both molecules is probably within the limits of experimental error; for example, the values of μ_2 and μ_3 in 10-bromotriptycyl iodoformate only differ by 1.3° from the expected value of 115.3°.

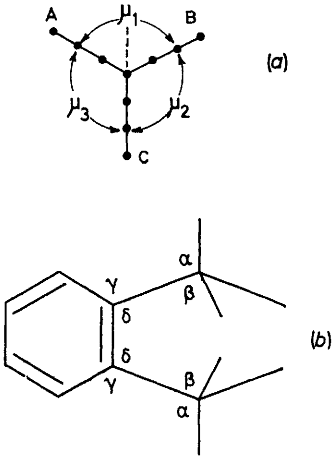

FIGURE 3 (see also Table 4) (a) View down the axis connecting atoms C(9) and C(10), showing angles between aromatic rings. The dotted line represents the plane of the iodoformate group. (b) Angles between sp^2 and sp^3 bonds

The mean values for the strained angles between the sp^2 and sp^3 bonds, [Figure 3(b)], agree well with those found for other triptycene derivatives (Table 4). The sp^2 bond angles γ and δ take up most of the strain, deforming by 7—8° in contrast to the angles α, which are only 2—3° less than the ideal value for tetrahedral hybrids. All the structures have $\alpha \simeq \delta$, implying that the exocyclic bonds at the bridgehead atoms are collinear, and parallel to the inner aromatic bonds; also $\gamma + \delta = 240°$, which indicates that each ring is coplanar with the bonds linking it to the bridgehead atoms.

DISCUSSION

One of the most conspicuous details of this structural study, is the carbon–iodine bond length of 1.98(3) Å, which is among the shortest hitherto observed for this bond. The data available in the literature show that variations in the length of the C–I bond result when the degree of saturation of the carbon atom varies: the greater the saturation, the longer the bond length. Some mean C–I bond lengths (Å) are:

Aromatic [14–20]	2.100 ± 0.019 *
Aliphatic [21–23]	2.215 ± 0.038 *
Olefinic [24, 25]	2.092 ± 0.005 †
Acetylenic [26]	1.99 ± 0.02 †

* Mean deviations. † Estimated errors.

Comparison of this range in bond lengths (0.225 Å) with those observed[27] for C–Br (1.94—1.795, 0.145 Å), C–Cl (1.757—1.635, 0.132 Å), and C–F (1.333—1.379, ~0), with varying degrees of saturation of the carbon atom illustrates the greater deformability of the valence orbitals of the heavier halogens, particularly iodine. In the case of the C–I bond, for example, this leads to an increase in electron density, or effective bond-order, as the carbon atom becomes less saturated.

However, the C–X (X = I, Br, or Cl) bond length of acetyl halides[27] and methyl chloroformate[28] are of the order of, or even slightly longer than those of the corresponding aliphatic C–X bond lengths. In these compounds the halogen atom is evidently restricted to form a pure σ-bond, presumably because the carbon π-orbitals which would be involved in a C–X bond of increased bond order are fully utilised in the localised orbitals of the carbonyl group.

In his review Kevill[4] predicts reasonable stability for iodoformates but attributes the formation of cholesteryl iodide from cholesteryl chloroformate and sodium iodide to be due to the instability of this secondary system and further, the possibility of neighbouring group participation in carbonium-ion formation. However,

TABLE 4

Comparison of bond and interplanar angles (°) [a] for triptycene derivatives (for key see Figure 3)

	α	β	γ	δ	μ_1	μ_2	μ_3
9-Bromotriptycene [b]	111.4	107.4	128.5	110.7	120	120	120
(+)-5-Dimethylamino-1,4-dimethoxytriptycene [c]		105.4	126.2	113.3	120.1	120.3	119.6
9-β-Chloroethyltriptycene [d]	111.8	106.6	127.5	113.4	131.0	118.0	111.0
10-Bromo-9-triptycyl iodoformate [e]	112.3	106.2	127.4	112.4	129.4	116.7	113.9

[a] The first four angles are mean values for each molecule; for 9-β-chloroethyltriptycene all angles are the mean values for the two independent molecules in the asymmetric unit. [b] Ref. 11. [c] Ref. 12. [d] Ref. 13. [e] Present work.

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not even 1-apocamphyl- or any other iodoformate, except the present one, has been isolated and characterised. Hence it is concluded that the structural features of 9-triptycyl iodoformate must account for its unexpected stability and C–I bond length which, in contrast to other carbonyl–halogen systems, more closely resembles the acetylenic rather than the saturated alkyl C–I distance. The crowded environment of the carbonyl oxygen atom [O(2), Figure 2], in which there are four contacts *ca.* 0.25 Å shorter than the expected van der Waals distance with carbon atoms from adjacent aromatic rings, suggests the possibility of an interaction between the oxygen orbitals and those of the aromatic ring systems, which could lead to the delocalisation of some of the carbonyl π-electron density into the ring orbitals. While perhaps not statistically very significant, the increase in the carbonyl bond length [1.22(4) Å, *cf.* mean of 1.17 ± 0.004 Å for acyl compounds,[27] and 1.19 ± 0.02 Å for methyl chloroformate [28]] is consistent with this interpretation. This decrease in π-electron density in the carbonyl bond could facilitate the role of the carbonyl carbon atom as π-acceptor with respect to the iodine atom, thus allowing an increase in the C–I bond-order comparable to that in the iodoacetylenes. Surprisingly, this stereo-electronic effect of the iodoformyl group did not lead to any observable change, (apart from the intensity and position of the bridgehead proton resonance) in the n.m.r. or u.v. spectra when compared with that of triptycene.

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