A Redetermination of the Crystal Structure of (+)-3-Bromocamphor and its Absolute Configuration

By F. H. ALLEN and D. ROGERS
(*Chemistry Department, Imperial College, London, S.W.7*)

THERE has been a need for some time for a reliable determination of the absolute configuration of a key terpene. (+)-3-Bromocamphor is a convenient choice, partly for its well established connections with other terpenes, and also because its crystal structure is already known. It was determined by Wiebenga and Krom,[1] who studied the isomorphous series 3-bromo-, 3-chloro-, and 3-cyano-camphor. They determined the x-, z-co-ordinates of all atoms from the [010] projections and refined them as far as was possible in 1946. The y-co-ordinates for cyano-camphor were estimated from a model and refined from the two other principal projections. No y-co-ordinates were found for any atoms in the halides.

Early in 1965 we attempted to use the published data of cyano-camphor and an estimated bromine position to determine the absolute configuration. 17 anomalous pairs of reflections were observed and 13 were in favour of the configuration proposed by Freüdenberg and Lwowski[2] and by Fredga and Meittenen[3]: the other four were noncommittal. The result was communicated privately to several individuals, with the warning that the assumptions made were too sweeping to guarantee the result and that it would need confirmation by a fresh three-dimensional study. Recently, however, Northolt and Palm[4] have published an exactly similar determination based on 9 anomalous pairs, and deduced the same absolute configuration. They give a useful outline of the configurational implication of this assignment.

We now report the result of a three-dimensional investigation of (+)-3-bromocamphor ($C_{10}H_{15}OBr$).

Crystal Data. Monoclinic. Space group $P2_1$. $a = 7{\cdot}35_9$ Å, $b = 7{\cdot}59_0$ Å, $c = 9{\cdot}12_0$ Å, $\beta = 94° 6'$. (From a combination of Weissenberg and powder diffraction data using least-squares techniques). $V = 508$ Å^3, $D_m = 1{\cdot}49 \pm 0{\cdot}03$ g. cm.$^{-3}$, $D_c = 1{\cdot}51$ g. cm.$^{-3}$ for $Z = 2$. $M = 231{\cdot}03$.

From Weissenberg photographs taken with Cu-K_α radiation, 782 reflections were estimated visually; a further 126 were unobserved and were included in the least-squares calculations at an intensity equal to two-thirds of the minimum observable. Anisotropic refinement was applied to C, Br, and O. Fifteen hydrogen atoms in calculated positions have been allowed for, and R now stands at 0·098.

Nineteen anomalous pairs of reflections in the $0kl$ zone were measured using a microdensitometer and the intensities compared with structure factors calculated allowing for the dispersion correction f'' of Br for Cu-K_α radiation.[5,6] The $1kl$ layer was also recorded at the same setting to establish a right-handed set of axes. All 19 pairs were unanimous in confirming the two previous assignments (see Figure 1) and show that the diagrams due to Wiebenga and Krom must be inverted.

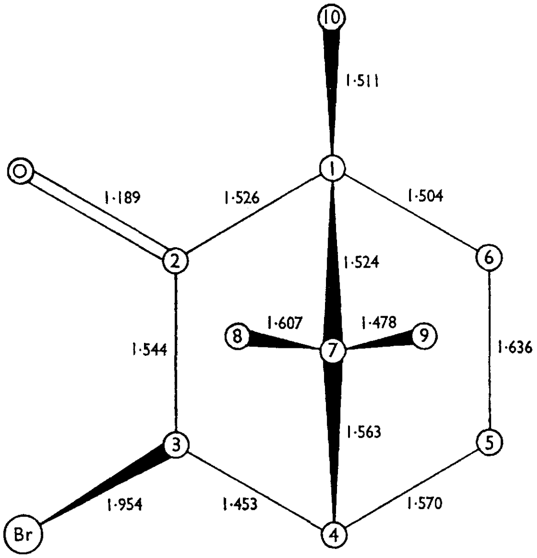

FIGURE 1. *Average* C–C *distances.*
(1) Ring atoms 1·539 ± 0·030 Å
(2) All C–C 1·536 ± 0·030 Å

This concurrence of three independent X-ray determinations is encouraging as it indicates that, contrary to the general impression, reasonably reliable assignments can be made fairly quickly for structures already in the literature without the need for thorough refinement. The Table shows that the average and maximum shifts (in Å) in the x-, y-, z-co-ordinates for the camphor framework given by Wiebenga and Krom are appreciable, but their x-, z-co-ordinates and our guesses at the y-co-ordinates were good enough to yield the correct configuration. Care and a strong concensus of anomalies are obviously necessary however.

TABLE

	x	*y*	*z*
Average shift (Å)	0·052	0·107	0·049
Maximum shift (Å)	0·110	0·440	0·128

The new bond lengths and average e.s.d.'s are shown in Figure 1. They agree well with Wiebenga and Krom's values. Bonds C(3)–C(4) and C(7)–C(9) are a little shorter than normal, and C(7)–C(8) and C(5)–C(6) are a little longer. This inequality in the two C(7)-methyl group bonds was also obtained by Wiebenga and Krom who also found that C(5)–C(6) was longer than average. A similar pattern of strain, the ring bonds on the substituted side being slightly shorter than average, while those opposite are longer, has been observed in 2-bromo-2-nitrosocamphane.[7]

Figure 2 shows the bond angles. Standard deviations range from 1·3 to 2·4°.

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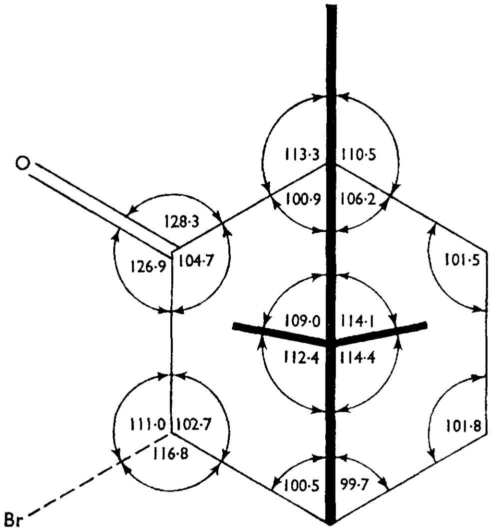

FIGURE 2. *Additional angles not shown on diagram.*

C(2)–C(1)–C(6) = 102·3°
C(3)–C(4)–C(5) = 113·5°
C(8)–C(7)–C(9) = 111·4°
C(7)–C(6)–C(10) = 121·6°

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