C–H · · · O Hydrogen Bonding

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THE shift of the ethynyl hydrogen stretching frequency of benzoylacetylene (Ph·CO·C⋮CH) from 3302 cm.$^{-1}$ in dilute carbon tetrachloride solution to 3225 cm.$^{-1}$ in the solid state has been attributed[1] to intermolecular hydrogen bonding between ethynyl C–H groups and carbonyl oxygen atoms. *o*-Bromo- and *o*-chloro-benzoylacetylene show similar spectral shifts. Relatively little is known[2] about C–H · · · O hydrogen bonding in the solid state and we are carrying out three-dimensional single-crystal *X*-ray analyses to determine the C–H · · · O distances in these compounds.

o-Bromobenzoylacetylene, C_9H_5OBr, $M = 209{\cdot}0$, m.p. 46°, orthorhombic, $a = 3{\cdot}94$, $b = 7{\cdot}30$,

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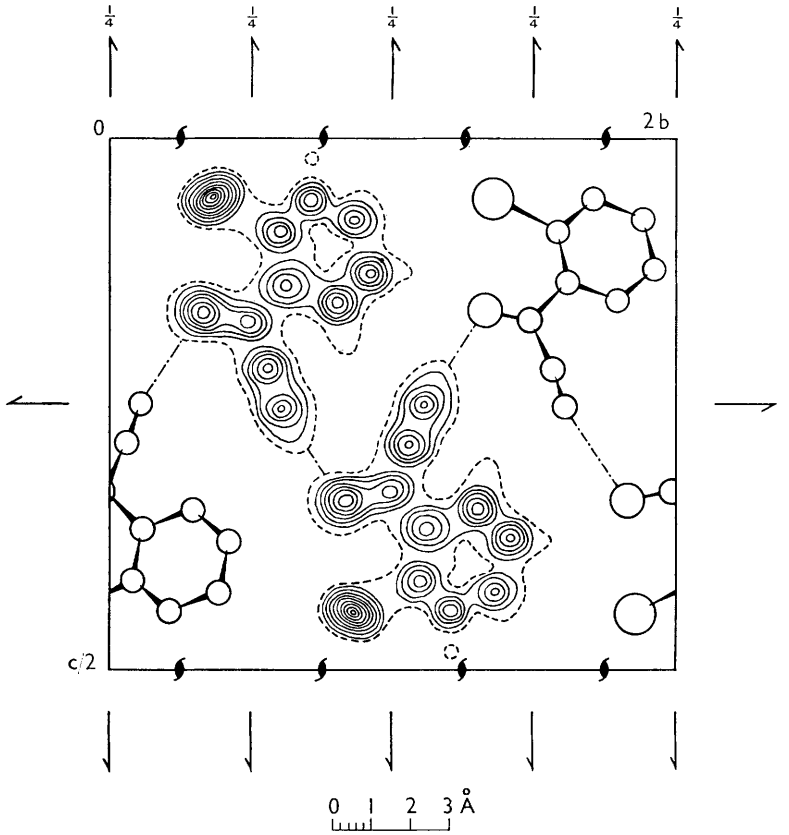
[1] J. Tyrrell, Ph.D. Thesis, Glasgow, 1963.
[2] D. J. Sutor, *Nature*, 1962, **195**, 68; *J. Chem. Soc.*, 1963, 1105.

$c = 27{\cdot}43$ Å, $Z = 4$, space group $P2_12_12_1$. The crystal structure was solved by way of the heavy atom and has been refined by electron-density syntheses and least-squares analyses.[3] At the present stage R stands at 8·0% for 550 observed reflexions.

structure on (100). Carbon–hydrogen distances have not been determined but if an ethynyl carbon–hydrogen distance of 1·06 Å is assumed[4] then the actual H · · · O separation will be 2·2 Å, which is considerably less than the van der Waals contact distance of 2·6 Å. The length of the



View of the structure of o-*bromobenzoylacetylene looking down* a. *Contour intervals are at* 1e Å^{-2} *except around the bromine atom where they are at* 5e Å^{-2}. *The one-electron contour is broken. Directions of the* C-H· · · O *hydrogen bonds are shown by dot-shaded lines.*

The distance between the ethynyl carbon atoms and carbonyl oxygen atoms involved in C–H · · · O hydrogen bonding is 3·260 ± 0·015 Å. All other distances are in accord with accepted values. The zig-zag arrangement of the intermolecular hydrogen bonding is clearly shown in the view of the

C–H · · · O bond in *o*-bromobenzoylacetylene indicates that it is comparatively weak, being comparable, at least on the basis of length, with the N–H · · · N (3·10 Å), O–H · · · Cl (3·08 Å), and N–H · · · Cl (3·21 Å) hydrogen bonds surveyed by Pimentel and McClellan.[5] In addition our value

[3] Computer programs devised by Dr. J. S. Rollett and Dr. J. G. Sime: see "Computing Methods and the Phase Problem in *X*-ray Crystal Analysis", ed. R. Pepinsky, J. M. Robertson, and J. C. Speakman, Pergamon Press, Oxford, 1961; J. S. Rollett, p. 87, J. G. Sime, p. 301.

[4] "Tables of Interatomic Distances and Configurations in Molecules and Ions", The Chemical Society, London, 1958.

[5] "The Hydrogen Bond," G. C. Pimentel and A. L. McClellan, W. H. Freeman and Co., San Francisco and London, 1960.

agrees with that found by Hassel in the ethyl ether–bromodichloromethane complex[6] and with those reviewed by Sutor.[2]

Further refinement is contemplated and work has been initiated[7] on the non-isomorphous chloro-compound, which, from preliminary studies in projection, seems to have a similar C–H · · · O distance.

(*Received, April 5th,* 1965.)

[6] O. Hassel, *Proc. Chem. Soc.*, 1957, 250; *Mol. Phys.*, 1958, **1**, 241.
[7] G. Ferguson, K. V. S. Islam, and J. M. Robertson, to be published.