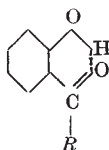


a broad band is associated with the structure where  $R$  is H or  $\text{CH}_3$ , but a sharp band is produced when  $R$  is OH or  $\text{O.CH}_3$ . With *o*-methoxybenzoic acid and *o*-hydroxybenzyl alcohol, the  $\text{C}=\text{O}$  group in the ring containing the hydrogen bond is replaced by  $\text{C}-\text{O}$ , and a sharp band results.



It is of interest to note that one-half of the dimer of acetic acid (Fig. 2) is very similar to part of the ring containing the hydrogen bond in *o*-hydroxyacetophenone, and the OH-absorption is much the same in the two cases, although that of the carboxylic acid has about three times greater intensity.

A. E. MARTIN

Sir Howard Grubb, Parsons and Co.,  
Optical Works, Walker Gate,  
Newcastle upon Tyne 6. May 4.

- <sup>1</sup> Buswell, Deitz and Rodebush, *J. Chem. Phys.*, **5**, 501, 726 (1937).  
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<sup>5</sup> Davies, *Ann. Rep. Chem. Soc.*, **43** (1946).  
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### Structure of Dimethyltriacetylene

CRYSTALS of pure dimethyltriacetylene<sup>1</sup>,  $\text{H}_3\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{CH}_3$ , sealed in a Lindemann glass tube, are sufficiently stable at room temperature for detailed X-ray analysis. The crystal structure has the space-group  $R\bar{3}m$  with one molecule in the rhombohedral unit cell. The centro-symmetrical molecule lies with its eight carbon atoms extended along the triad axis, and four parameters suffice to define their positions completely. These parameters have been determined by a Fourier synthesis of the ( $h0\bar{h}l$ ) structure factors; the atomic centres were located by the differential method with application of termination-of-series corrections<sup>2</sup>. The standard deviation of the bond-lengths is at present estimated to be 0.015 Å., and it is hoped that further work now in progress may increase the accuracy of the analysis. The bond-lengths obtained are compared with those from related molecules in the accompanying table.

BOND-LENGTHS IN ACETYLENIC MOLECULES

Substance	$-\text{C}\equiv\text{C}-$	$\equiv\text{C}-\text{C}\equiv$	$\equiv\text{C}-\text{CH}_3$	Method
Dimethyltriacetylene	1.19, A.	1.38, A.	1.46, A.	X-ray
Acetylene	1.204	—	—	Spec <sup>3</sup>
Methylacetylene	—	—	1.462	Spec <sup>4</sup>
Dimethyldiacetylene	1.20	1.38	1.47	Elect. diff. <sup>5</sup>
Diacetylene	1.19	1.36	—	Elect. diff. <sup>5</sup>
Diphenyldiacetylene	1.18	1.39	—	X-ray <sup>6</sup>
Diacetylenedicarboxylic acid	1.18,	1.33	—	X-ray <sup>7</sup>

The triple bond-lengths in this table show very close agreement. The lengths of the conjugated single bonds, which are of particular interest because of their anomalous force constants in diacetylene and dimethyldiacetylene<sup>5</sup>, appear to vary considerably, and unless this bond is unusually sensitive to environment our measurement is inconsistent with the value reported for diacetylene-dicarboxylic acid<sup>7</sup>. The

value for the hyperconjugated single bond-lengths in the dimethyltriacetylene is the same within experimental error as the spectroscopic value for methylacetylene.

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G. A. JEFFREY  
J. S. ROLLETT

Chemistry Department,  
University, Leeds.

May 11.

- <sup>1</sup> Jones, Tilden Lecture, *J. Chem. Soc.*, 754 (1950).  
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### Raman Effect of the Isomers of Benzene Hexachloride

IN the course of our research programme on the structure of molecules, we have photographed the Raman lines of the pure alpha, beta, gamma and delta isomers of benzene hexachloride ( $\text{C}_6\text{H}_6\text{Cl}_6$ ) dissolved in benzene. The lines were photographed with a Steinheil GH three-prism spectrograph specially fitted for Raman work (collimator,  $f = 195$  mm.; camera,  $f = 255$  mm.). The lines were excited by the mercury line 4358 Å. by means of a Heraeus No. S700 lamp.

The following Raman lines of the pure isomers were observed:

Alpha:	285, 310, 340, 400, 555, 655, 710, 795, 860 $\text{cm}^{-1}$
Beta:	265, 305, 375, 390, 555, 670, 730, 855 $\text{cm}^{-1}$
Gamma:	325, 345, 390, 485, 860, 690, 785, 890 $\text{cm}^{-1}$
Delta:	300, 475, 555, 755, 790 $\text{cm}^{-1}$

Of these the following frequencies were selected, the intensities of which were not influenced by the solvent: 710 (alpha), 730 (beta), 690 (gamma) and 475  $\text{cm}^{-1}$  (delta), and were used for the determination of the isomer content of an industrial product. The intensities of these lines, which were measured on a Leeds and Northrup microphotometer, were compared with one another and with a suitable benzene line.

The preliminary experiments have shown that it is possible to estimate the isomer constitution of technical benzene hexachloride (with an accuracy of about  $\pm 4$  per cent) by means of the Raman effect.

A more complete description will be given elsewhere of the preparation of the pure isomers, the analysis procedure, the structure of the  $\text{C}_6\text{H}_6\text{Cl}_6$  molecule and of a characteristic intensity and frequency change observed in mixtures.

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S. M. NAUDÉ  
H. VERLEGER

National Physical Laboratory,  
Pretoria.

H. L. DE WAAL

Chemistry Department,  
University of Pretoria.