162. *The Infra-red Spectrum of Phenylacetylene.*

By H. W. Thompson and P. Torkington.

The infra-red absorption spectrum of phenylacetylene has been measured between 3 and 20 μ. The results have been correlated with data from the Raman spectrum, and a consideration of several related molecules suggests a series of magnitudes for some of the vibrations of the phenyl nuclear skeleton.

The Raman spectra of several substituted acetylenes including phenylacetylene have been measured by Murray and Cleveland (*J. Amer. Chem. Soc.*, 1938, **60**, 2664; 1940, **62**, 3185; *J. Chem. Physics*, 1940, **8**, 133), who have also measured the infra-red absorption spectrum of phenylmethylacetylene and compared the observed absorption frequencies with the Raman intervals. We have recently measured the infra-red spectrum of phenylacetylene, which can now be correlated with the Raman spectrum. With molecules of this degree of complexity there are so many fundamental vibration frequencies that a satisfactory normal co-ordinate treatment is at present impracticable, and attempts to correlate the frequencies with motions of particular parts of the nuclear skeleton must in the first instance be based upon correlation of the data with a series of closely related molecules.

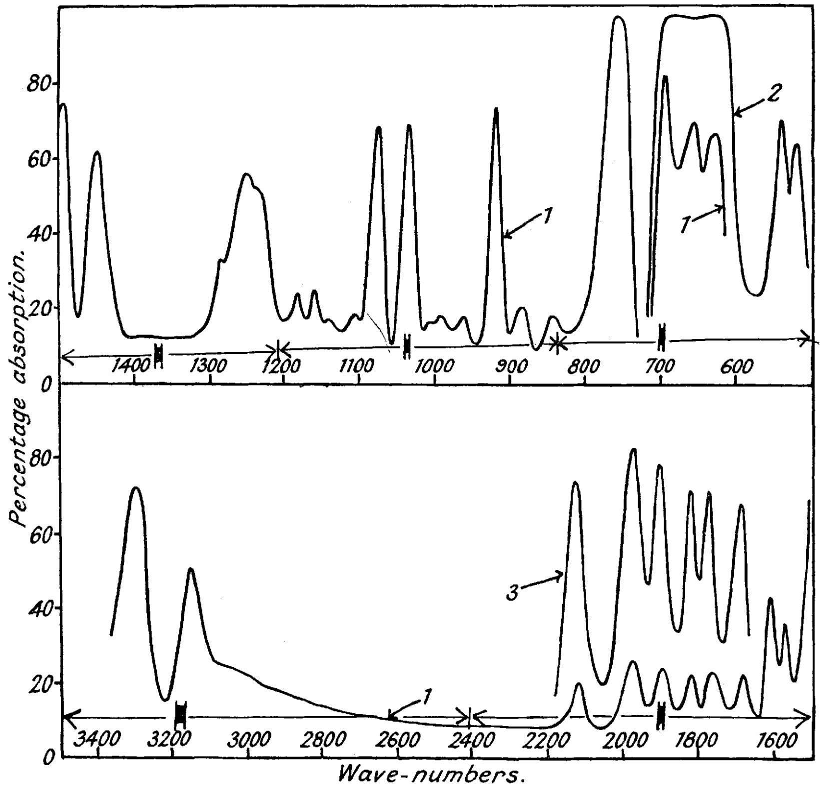
The phenylacetylene was a synthetic product, kindly supplied by the Research Department of I.C.I. Ltd. (Dyestuffs Division). It was distilled before use; b. p. 142°. The liquid was studied in absorption cells about 0·05, 0·1, and 0·3 mm. thick, made by separating a pair of polished rock-salt or sylvine plates with a metal washer. A few measurements on some of the strongest bands were also made with the vapour, low pressures being used in a cell 20 cm. long. The spectrometers used have already been described by us (*Proc. Roy. Soc.*, in the press).

Results and Discussion.—The absorption curves for the range 500—3300 cm.$^{-1}$ (20—3 μ) are shown in the figure, and Table I lists the positions of the bands (in wave-numbers), together with the frequencies obtained from the Raman spectrum by Murray and Cleveland. There is a marked correspondence between the infra-red and the Raman data, similar to that found for phenylmethylacetylene. As might have been expected, the frequencies which are most strongly absorbed in the infra-red tend to be relatively weak in the Raman effect, and *vice versa*.

TABLE I.

Infra-red.	Raman.	Infra-red.	Raman.	Infra-red.	Raman.	Infra-red.	Raman.	Infra-red.	Raman.
	164(6)	758 s	760(5)	1074 s		1282 w	1281(1)	1770 w	
	353(4)	842 w		1103 w			1337(1)	1820 w	
	465(3)	883 w		1140 w			?1380(1)	1900 w	
518 m	517(2)	915 s		1156 w	1155(2)	1450 s	1447(1)	1972 w	
535 m	530(3)	956 w		1180 w	1176(4)	1493 s	1489(2b)	2128 w	2113(10)
625 m	621(4b)	990 w			1196(6)	1582 w			3066(8)
655 m		1002 w	1001(7)	1230 m	1230(1)	1608 m	1601(9)	3155 m	3142(1)
693 s		1030 s	1027(2)	1250 m		1685 w		~3300 s	3288(3)

Now with both phenylacetylene and phenylmethylacetylene there will be a set of frequencies above about 1400 cm.$^{-1}$ which are determined essentially by vibrations of C–H bonds and the $C\equiv C$ link. Thus the valency vibrations of C–H bonds will lie around 3000 cm.$^{-1}$, and that of the $C\equiv C$ bond at about 2200, while C–H deformations will give rise to frequencies in the region of 1400 cm.$^{-1}$. The other normal modes, which will nearly all involve motions within the phenyl nucleus, will have values below about 1400 cm.$^{-1}$. We may therefore compare the values found in this range for phenylacetylene with those of phenylmethylacetylene. The five most intense infra-red bands of the former lie at 693, 758, 915, 1030, and 1074 cm.$^{-1}$. There is a striking parallelism with the most intense bands of the latter, which lie at 702, 754, 909, 1024, and 1064, cm.$^{-1}$, although another strong band is found at 526 cm.$^{-1}$. The last band might be correlated with one or other of the bands found with phenylacetylene at 518 and 535 cm.$^{-1}$, but this is less certain. We might therefore infer that the five principal bands just referred to are associated with vibrations of the phenyl nucleus.



Phenylacetylene : (1) 0·05 *mm.*, (2) 0·10 *mm.*, (3) 0·30 *mm.*

As a further test of this, comparison can now be made with the spectra of other related molecules. Thus, the most intense bands in the spectrum of styrene below 1400 cm.$^{-1}$ (Thompson and Torkington, *Proc. Roy. Soc.*, in the press) lie at 700, 775, 911, 993, 1025, and 1083 cm.$^{-1}$. It was shown previously that two of these, *viz.*, 911 and 993 cm.$^{-1}$, are definitely associated with motions of the vinyl part of the nuclear skeleton. On the other hand, the band at 911 cm.$^{-1}$ is abnormally broad, and may well comprise a close pair at, say, 905/910 cm.$^{-1}$. This would leave as the unexplained strong bands 700, 775, 905, 1025, and 1083 cm.$^{-1}$, which correspond excellently with the five magnitudes found for the phenylacetylenes.

The correlation can be examined further by reference to the infra-red spectra of benzene and alkylbenzenes. These spectra and their correlation will be published elsewhere (Sutherland, Thompson, Turner, and others), but we may note that the main infra-red bands below 1400 cm.$^{-1}$ occur at the following frequencies :

Toluene	730	895	1035	1078	Propylbenzene	740	905	1030	1090
Ethylbenzene	745	905	1035	1090	*iso*Propylbenzene	762	905	1030	1082

With the propylbenzenes there are several other strong bands which appear to be more closely connected with oscillations in the side chain. We may also note that benzene has its most intense bands at 670 and 1035 cm.$^{-1}$.

All this evidence supports the argument that the following frequencies (cm.$^{-1}$) are associated with motions within the phenyl nucleus :

Phenylacetylene	758	915	1030	1074
Phenylmethylacetylene	754	909	1024	1064

It is possible that the frequencies 693 of phenyl- and 702 of phenylmethyl-acetylene relate to deformations involving the side-chain skeleton. On the other hand, if this were so, we might expect the analogue with styrene to be markedly affected by the change from triple to double carbon–carbon bond, whereas it lies at 700.

A more detailed discussion of these correlations will be deferred until data on related molecules are available, and the spectra of some of the saturated aromatic hydrocarbons have been measured between 14 and 20 μ.

THE PHYSICAL CHEMISTRY LABORATORY, OXFORD. [*Received, May 25th,* 1944.]