51. *The Infra-red Spectra of Carcinogens. Part II. Polynuclear Hydrocarbons.*

By S. F. D. ORR and H. W. THOMPSON.

Vibration spectra of some polynuclear aromatic hydrocarbons, which are of interest in cancer research, have been measured. Attempts have been made to correlate spectral features with molecular structure, particularly with regard to the vibrations of C—H bonds in substituted aromatic rings.

IN continuation of work described in the preceding paper, we now give results for the spectra of some polynuclear hydrocarbons and a few related molecules. As before, the data may be useful for analytical work, and as regards the correlation of spectrum with molecular structure it was interesting to discover how far the rules given in the previous paper for the identification of aromatic nuclei substituted in different positions are applicable when the substituent bonds are themselves part of other rings of the ring-system.

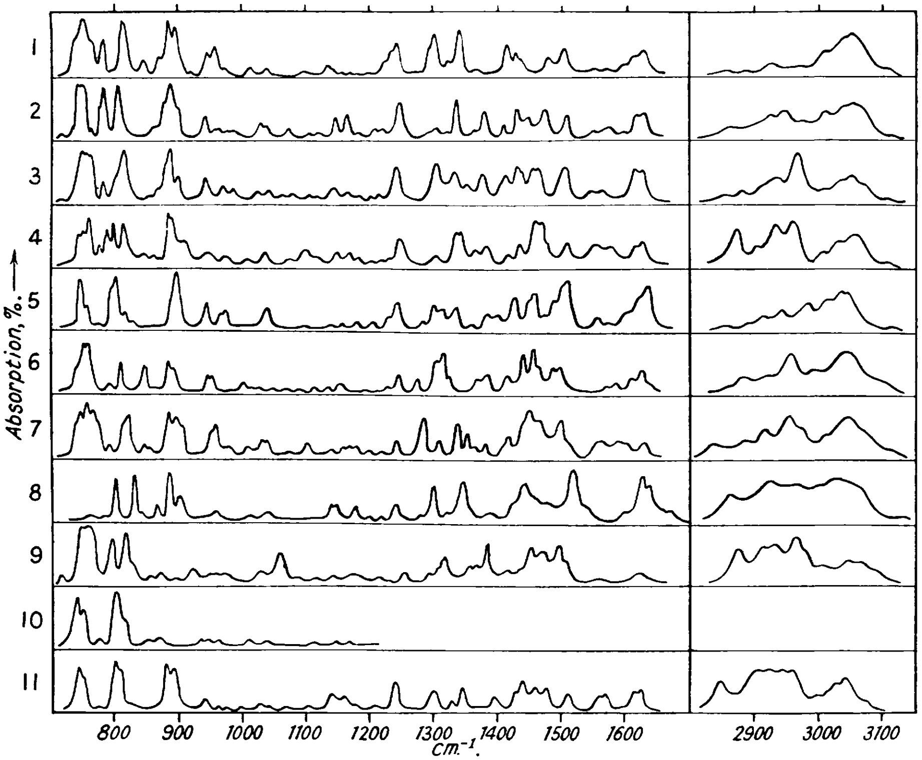
The experimental methods were as described in the preceding paper, except that most of the spectra were measured on a Perkin Elmer 12 C spectrometer, with a prism of rock salt or lithium fluoride. The compounds were measured as thin solid films made by melting a small sample and pressing it between rock-salt plates. In the case of 9 : 10-dihydroanthracene, which tends to decompose on melting, a paste in paraffin was used.

The spectra are shown in Figs. 1, 2, and 3. The broad features of the spectra of the 1 : 2-benzanthracenes (Fig. 1) are a number of strong bands between 700 and 900 cm.$^{-1}$, a region of comparative transparency at 900—1200 cm.$^{-1}$, and a complex arrangement of bands between 1200 and 1700 cm.$^{-1}$. The vibrations giving rise to the intense bands at 700—900 cm.$^{-1}$ will include the out-of-plane deformations of C—H bonds in the substituted aromatic rings. It is clear that in the present set of compounds the situation is more complex than with the stilbenes described in the preceding paper, but several points emerge.

All the compounds in Fig. 1, except 2′ : 6-dimethyl-1 : 2-benzanthracene, contain an aromatic ring which is 1 : 2-disubstituted only. It is therefore noticeable that all except this compound have a strong band around 750 cm.$^{-1}$, in the characteristic position for an *ortho*-disubstituted ring, although the small shift from one molecule to another is rather bigger than usual. This rule for 1 : 2-disubstitution also appears to hold for the other compounds in Figs. 2 and 3, except 9 : 10-dihydroanthracene and anthracene itself, but in many cases there is a shift of 10 cm.$^{-1}$ to higher or lower frequencies.

FIG. 1.

1 : 2-*Benzanthracenes.*



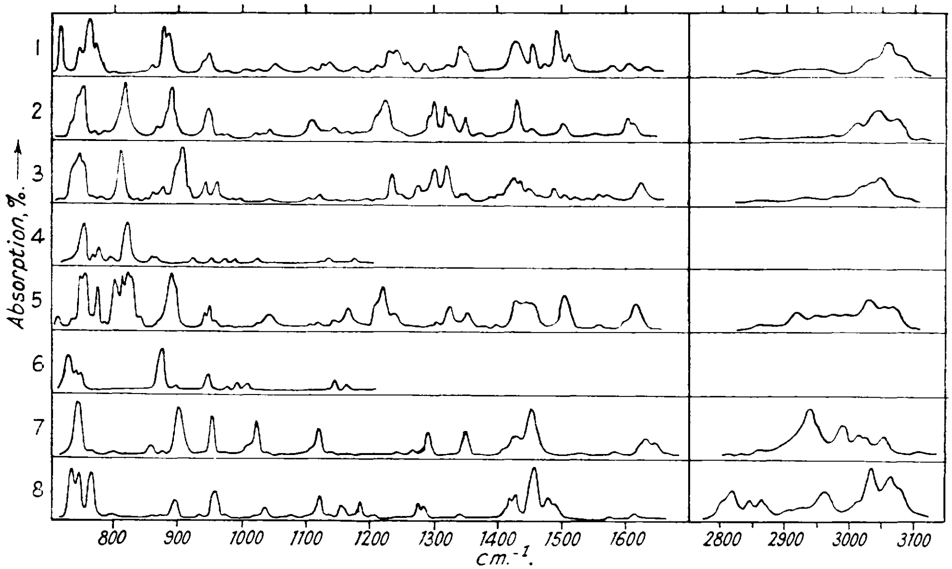
(1) 1 : 2-*Benzanthracene.* (2) 5-*Methyl*-1 : 2-*benzanthracene.* (3) 5-*Ethyl*-1 : 2-*benzanthracene.* (4) 5-n-*Propyl*-1 : 2-*benzanthracene.* (5) 7-*Methyl*-1 : 2-*benzanthracene.* (6) 9-*Methyl*-1 : 2-*benzanthracene.* (7) 1′-*Methyl*-1 : 2-*benzanthracene.* (8) 2′ : 6-*Dimethyl*-1 : 2-*benzanthracene.* (9) 9 : 10-*Dimethyl*-1 : 2-*benzanthracene.* (10) 6 : 9 : 10-*Trimethyl*-1 : 2-*benzanthracene.* (11) 5 : 6-cyclo*Penteno*-1 : 2-*benzanthracene.*

Another noticeable characteristic of the benzanthracenes (Fig. 1) is a strong band near 890 cm.$^{-1}$, which occurs in all cases unless there is substitution also in the 9 : 10-positions. This suggests that the central ring can be regarded as being substituted in the 1 : 2 : 4 : 5-positions. For ordinary 1 : 2 : 4 : 5-tetrasubstituted benzene derivatives, a band has previously been found at about 875 cm.$^{-1}$. It should be noted however that 9-methyl-1 : 2-benzanthracene has a weaker band at 890 cm.$^{-1}$. Among the other compounds of Figs. 2 and 3 with one exception all those with an unsubstituted middle anthracene ring show the band near 890 cm.$^{-1}$, and with one exception it is absent from molecules with essentially different structures, such as a reduced middle anthracene ring. The exception is again 9 : 10-dihydroanthracene, which shows a band near 890 cm.$^{-1}$, although this is weaker than usual.

The other strong bands between 700 and 900 cm.$^{-1}$ are more difficult to correlate. One possible regularity is suggested by the strong bands at 800—810 cm.$^{-1}$ found in all compounds (except acridine derivatives) containing 1 : 2 : 3 : 4-substitution. Although simple 1 : 2 : 3 : 4-tetrasubstituted benzene derivatives have not been available to enable us to determine the

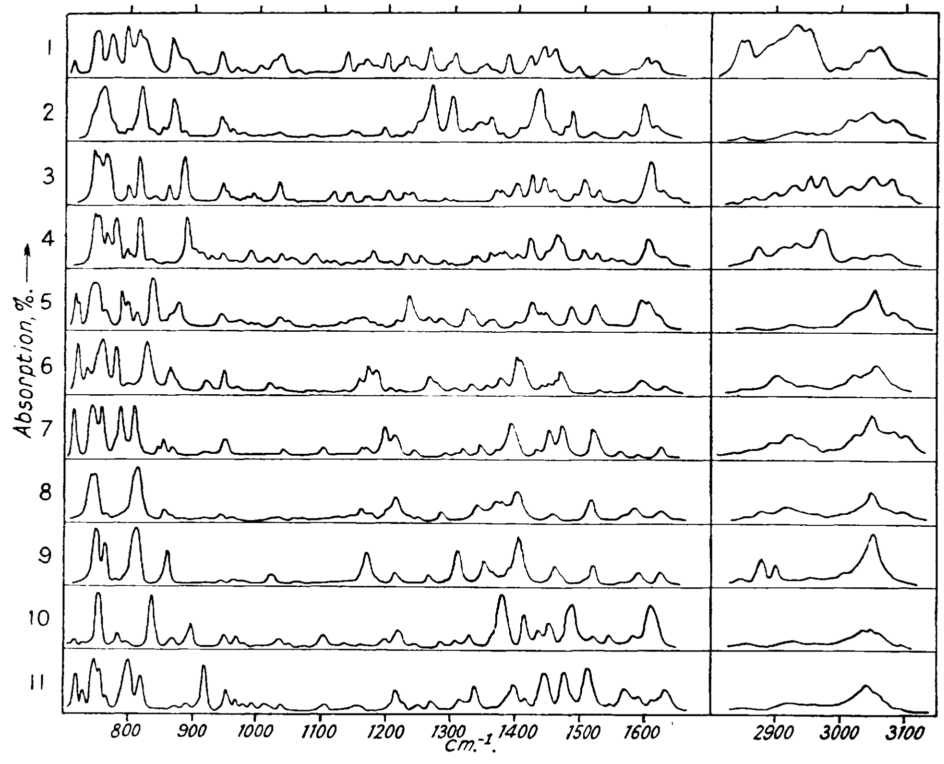
FIG. 2.

Dibenzanthracenes and anthracenes.



(1) 1 : 2-3 : 4-*Dibenzanthracene.* (2) 1 : 2-5 : 6-*Dibenzanthracene.* (3) 1 : 2-6 : 7-*Dibenzanthracene.* (4) 9 : 10-*Dihydro*-1 : 2-5 : 6-*dibenzanthracene.* (5) 3′-*Methyl*-1 : 2-5 : 6-*dibenzanthracene.* (6) *Anthracene.* (7) 2 : 3-*Dimethylanthracene.* (8) 9 : 10-*Dihydroanthracene.*

FIG. 3.



(1) 1 : 2-cyclo*Pentenophenanthrene.* (2) *Chrysene.* (3) 2-*Methyl*-3 : 4-*benzphenanthrene.* (4) 2-iso*Propyl*-3 : 4-*benzphenanthrene.* (5) 1 : 2-5 : 6-*Dibenzphenanthrene.* (6) 1 : 2-*Benzfluorene.* (7) 3 : 4-*Benzfluorene.* (8) 1 : 2-5 : 6-*Dibenzfluorene.* (9) 1 : 2-7 : 8-*Dibenzfluorene.* (10) 3 : 4-6 : 7-*Dibenzacridine.* (11) 1 : 2-8 : 9-*Dibenzacridine.*

characteristic C—H out-of-plane frequency in this type, we might argue by extrapolation from the results with the other compounds that it would have a value close to that just found.

A less prominent band which seems to persist throughout the 1 : 2-benzanthracenes lies near 1240 cm.$^{-1}$, although here a few small deviations occur which, taken with the weaker nature of the band, obscure the position.

In the region 2800—3100 cm.$^{-1}$ these compounds have bands due to the C—H stretching vibrations. Beyond the general and expected result that the aromatic C—H vibrations give bands at 3000—3100 cm.$^{-1}$ and the aliphatic C—H vibrations at lower frequencies, 2850—2950 cm.$^{-1}$, no very significant conclusions can at present be drawn.

We are again indebted to Prof. G. A. R. Kon, F.R.S., for most of the pure hydrocarbon examined.

THE PHYSICAL CHEMISTRY LABORATORY, OXFORD. [*Received, June 30th*, 1949.]