Infrared spectra of photodimers of anthracene, benzo[a]anthracene, and tetracene

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Infrared spectra of the photodimers of anthracene, anthracene-d_{10}, tetracene, and benzo[a]anthracene are reported in the region 4000–200 cm^{-1}. An attempt is made to correlate the observed bands with the proposed structure of the anthracene dimer. The infrared spectra indicate that the dimers of benzo[a]anthracene and tetracene have similar structures.

Introduction

Anthracene is known (1, 2) to form a photodimer when its deaerated solution in cyclohexane or in benzene is exposed to ultraviolet radiation. X-Ray (3) and electronic spectral (2) data show that in dianthracene the two anthracene molecules are joined at their meso positions. The top and bottom of the central rings are bent forwards and the outer rings backwards as a result of electrostatic repulsion. Mustafa and co-workers (4) prepared the dimer of benzo[a]anthracene and more recently Birks (5), Livingston (6), and their co-workers have reported the formation of ditetracene under similar experimental conditions. It was thought of interest to study the infrared spectra of these dimers and correlate the spectral results with the proposed structures. The infrared spectra of anthracene, benzo[a]anthracene, tetracene, and many other polynuclear aromatic hydrocarbons were studied by Cannon and Sutherland (7). Attempts have also been made to assign the infrared and Raman spectra of anthracene by carrying out a normal coordinate analysis (8) and polarized radiation (9) studies.

We have now prepared the photodimers of anthracene, anthracene-d_{10}, benzo[a]anthracene, and tetracene. The infrared spectra of these dimers are discussed using the available (7–9) assignments of monomers.

Experimental

Zone refined anthracene and anthracene-d_{10} were obtained from Dr. W. G. Schneider of the National Research Council of Canada and recrystallized pure tetracene was obtained from Professor M. S. Newman of Ohio State University, to whom our sincere thanks are due. Benzo[a]anthracene was purchased from Eastman Organic Chemicals. The anthracenes and tetracene were used without further purification. Benzo[a]anthracene was recrystallized from alcohol before use. Spectrograde benzene and cyclohexane were used without further purification. The dianthracenes were prepared by irradiating saturated cyclohexane solutions (1 g/l) of anthracene for 7 to 8 h by a Hanovia high pressure mercury–xenon arc type 6-B-1. Dimers of benzo[a]anthracene and tetracene were prepared by irradiating their saturated solutions in benzene using a 1 kW tungsten lamp for 3 to 4 days. The solutions were flushed with dry nitrogen for 20–30 min before irradiating. The reactions were carried out in quartz tubes kept in Pyrex water jackets to avoid unnecessary heating of the samples. The crystalline precipitates were washed 10 to 12 times with the solvents which were used and dried in a vacuum desiccator. The ultraviolet spectra of the dimers show that di(benzo[a]anthracene) and ditetracene have monomer impurities which may not be more than 1%. The infrared spectra were recorded on a Perkin–Elmer 621 spectrophotometer. The samples were handled in the form of potassium bromide pellets, Nujol mulls, or solutions in 2.5 cm long cells with sodium chloride windows.

Results and Discussion

The infrared spectra of dianthracene and dianthracene-d_{20} are shown in Figs. 1 and 2. The band positions of the anthracene monomer and dimer and dianthracene-d_{20} are listed in Table I. Results from spectra taken in both KBr pellets and Nujol mulls are listed. The spectra in the C—H region were taken in saturated carbon tetrachloride and carbon disulfide solutions too.

The infrared spectrum of dianthracene shows 7 to 8 well defined bands in the C—H region (Table I). The bands are of medium or weak intensity and are observed almost at the same positions in KBr pellets and in the solution spectra. Two of the bands are considerably below the aromatic C—H stretching region (2945 and 2921 cm^{-1}). The spectra in carbon tetrachloride and carbon disulfide solutions in this region are ill defined due to strong solvent absorption.

According to the available X-ray (3) and
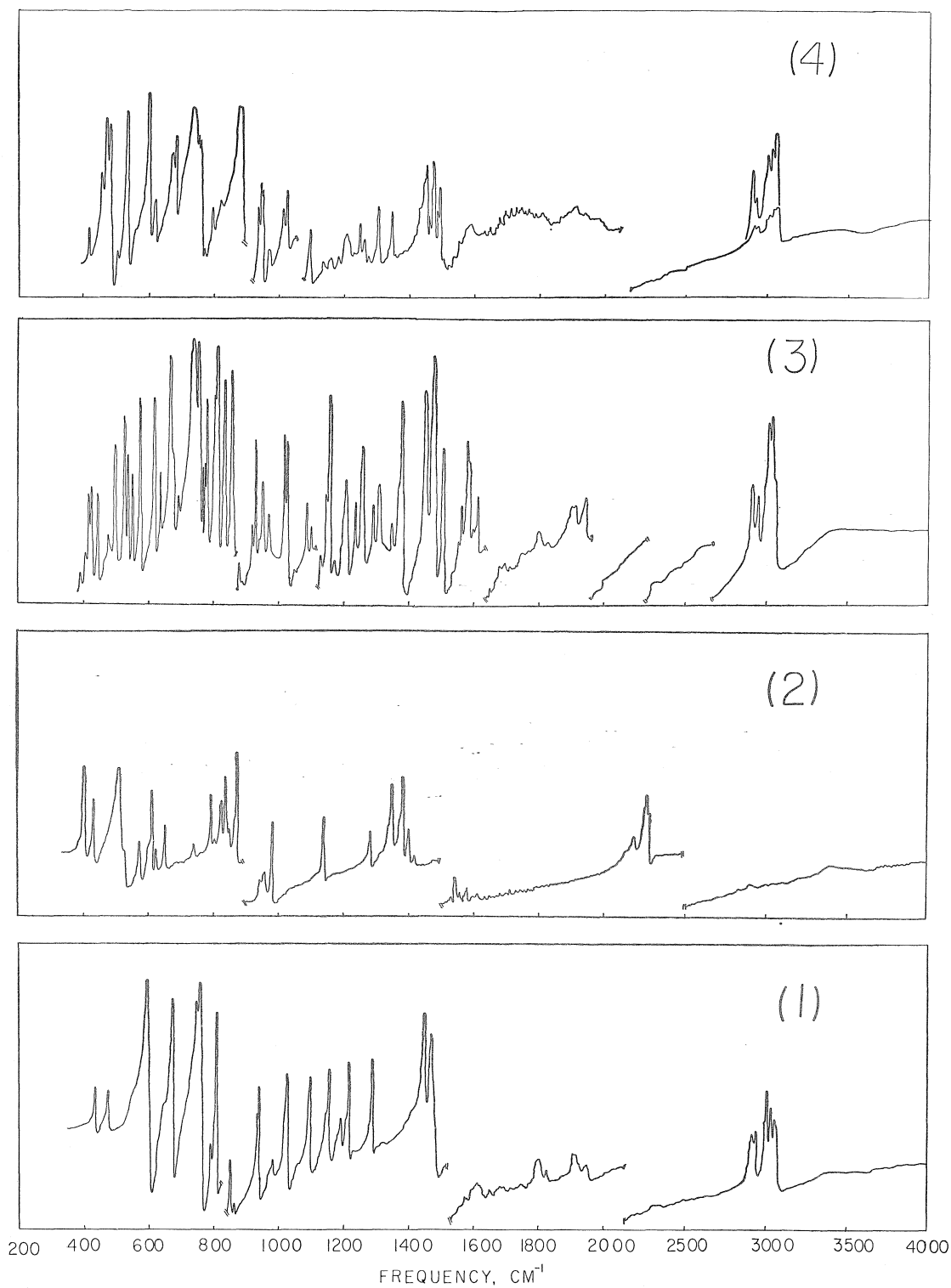
FIGS. 1–4.   Infrared spectra of photodimers of (1) anthracene, (2) anthracene-d_{10}, (3) benzo[a]anthracene, and (4) tetracene in KBr pellet.

TABLE I

Infrared absorption bands of dianthracene and dianthracene-d_{20}*

	Band positions of			
	dianthracene in		dianthracene-d_{20} in	
anthracene in KBr pellet	KBr pellet	Nujol mull†	KBr pellet	Nujol mull
		3090 vw	2290 msh	2282 msh
3100 w	3070 msh	3070 wsh	2267 m	2275 msh
3080 wsh	3059 m	3060 m	2260 msh	2265 m
	3035 m	3035 m	2255 msh	2255 msh
3045 s	3012 m	3015 m		2235 vwsh
3020 ssh	3000 msh	3000 wsh	2190 w	2190 w
	2945 m			2145 w,b
3000 msh	2921 m	2905–2940 vb,w		
	2905 wsh			
1923 m,b	1948 w	1950 vw		
	1908 w	1915 vvw,b		
	1830 vw	1830 vvw		
1800 mb	1800 w	1800 vvw		
1700 w,b		1680 vvw		
		1650 vvw	1575 vw	1572 vw
1613 w	1620 vw	1620 vvw	1545 vw	1545 vw
1560 w			1420 vw	
1520 wb	1575 vw		1402 w	1400 w
1444 m	1471 m		1385 m	1385 m
1440 msh	1465 msb		1375 msh	1365 msh
1390 w	1453 m		1351 m	1350 m
1340 w	1445 msh		1340 w,sh	1340 wsh
1310 mb			1283 m	1287 m
1265 w	1292 m	1290 m	1270 wsh	1270 wsh
1260 m	1220 m	1215 m		
1255 w	1205 wsh	1205 vw		
			1141 m	1140 m
	1195 w	1190 w	984 m	980 m
1164 m	1180 wsh	1180 vw	959 w	960 w
1144 w	1160 m	1165 msh	945 vw	945 vw
		1162 m	876 m	873 m
1122 m	1150 msh			
		1145 wsh	865 wsh	865 wsh
			850 vw	850 w
	1102 m	1100 m	845 w	840 wsh
	1095 msh	1095 wsh	838 m	837 m
995 m	1030 m	1025 m	827 w	825 w
975 w	1020 msh	1020 w	805 vw	805 vw
970 w	985 w	950 vw	794 m	793 m
		965 vw	739 w	740 w
950 s				
925 w	944 m	945 m		690 vw
900 m	939 m	940 w	653 m	652 m
884 s	868 w	865 w	622 w	620 w
850 m	856 w	855 wsh	611 m	608 m
		850 w	600 wsh	595 vw
	815 s	810 s	575 m	570 m
			530 wsh	
	797 w	790 w	508 s	515 vs
				490 wsh
765 vw		770 wsh		
750 vw	762 vs	760 vs	431 m	425 m
740 m	753 s	750 s	402 s	400 s
730 s	745 msh	745 s		
725 vs		735 wsh		
645 vw	677 s	675 s		
	665 msh			
600 m	650 msh	650 w		
560 vw	599 s	600 m		
		595 vs		
465 s	474 m	470 m		
455 s	435 m	430 m		
		340 w		
		312 w		

*v = very; w = weak; m = medium; s = strong; sh = shoulder; b = broad.
†The 3090–2905 cm^{-1} range reported is from the spectra in carbon disulfide and carbon tetrachloride solutions.

electronic spectral (2) results, the highest symmetry dianthracene can have is D_{2h}. By simple group theoretical considerations (10) using internal coordinates, the 20 C—H stretching vibrations can be shown to belong to the following symmetry species

$$\Gamma_D\nu(C—H) = 3A_g + 2B_{1g} + 2B_{2g} + 3B_{3g} \\ + 2A_u + \underline{3B_{1u}} + \underline{3B_{2u}} + \underline{2B_{3u}}$$

B_{1u}, B_{2u}, and B_{3u} are the only infrared active species and are underlined. In the proposed structure of dianthracene (2) not all 20 protons are aromatic. Four protons in the meso positions of the monomer anthracene units become tertiary aliphatic protons. The normal vibrations due to these 4 C—H bonds can be shown to belong to the A_g, B_{3g}, $\underline{B_{1u}}$, and $\underline{B_{2u}}$ species. Thus 2 out of 4 aliphatic C—H vibrations are expected to be infrared active. The 10 C—H stretching vibrations in the anthracene monomer have similarly been shown to belong to the A_g, B_{1g}, B_{2u}, and B_{3u} species as follows:

$$\Gamma_M\nu(C—H) = 3A_g + 2B_{1g} + \underline{3B_{2u}} + \underline{2B_{3u}}$$

The 5 infrared active vibrations ($3B_{2u}$ and $2B_{3u}$) have been (8) assigned to the 5 bands appearing in the range 3100–2990 cm^{-1} in the anthracene spectrum. Based on the above arguments we assign the 2 low lying bands at 2945 and 2921 cm^{-1} to the aliphatic C—H stretching vibrations. The remaining 5 bands at 3070, 3059, 3035, 3012, and 3000 cm^{-1} can thus be assigned to the aromatic, =C—H stretching vibrations. It can be seen that in the spectrum of dianthracene-d_{20} also, though the bands are not as well resolved, the 2 groups of bands are present in the C—D stretching region. This gives additional support to the proposed structure of dianthracene.

The C—C stretching vibrations are quite weak as usual, and a detailed discussion of them is not warranted. About 10–15 bands of very weak to medium intensity are found in the region 2000 to 1300 cm^{-1}. Weak bands from 1700 to 2500 cm^{-1} are usually assigned to overtones and combinations (11).

The lower frequency region is more interesting. There are 4 very strong bands and about 10 medium strong bands in the spectrum of dianthracene in the region 1300–200 cm^{-1}. Dianthracene-d_{20} has a similar spectrum. While surveying the bands in Table I it appears that the

bands at 1215, 1100, 1025, 810, and the broad band at 760 cm^{-1} with shoulders at 750 and 745 cm^{-1} in dianthracene experience an isotopic shift when compared to the spectrum of dianthracene-d_{20}. The $\nu(H)/\nu(D)$ ratio varies between 1.2 and 1.4. All other bands undergo only a very slight shift, the $\nu(H)/\nu(D)$ being 1.1 for the most shifted and 1.01 for the least shifted band. It can therefore be concluded that the bands with a shift of the order of 1.2 to 1.4 might belong to the C—H in-plane or out-of-plane bending vibrations and the other bands to the C—C bending motions or skeletal distortions. As can be seen from Fig. 1 the bands at 810 and 760 cm^{-1} are very strong, a characteristic of the C—H out-of-plane bending vibrations. The in-plane bendings are usually weaker. Anthracene shows 3 C—H out-of-plane bending vibrations

$$\Gamma_M\nu(C—H) = 2B_{2g} + 3B_{3g} + 2A_u + \underline{3B_{1u}}$$

at 954, 884, and 727 cm^{-1} in solutions (9). Another band at 870 cm^{-1} has been reported in the crystal spectrum (9). This is assumed to be due to an infrared inactive vibration, A_u, which is allowed by site symmetry. The dimer should have 6 infrared active vibrations due to out-of-plane aromatic C—H deformations and 2 infrared active out-of-plane aliphatic C—H deformation vibrations

$$\Gamma_D\nu(C—H)Ar = 2A_g + 2B_{1g} + 2B_{2g} + 2B_{3g} \\ + 2A_u + \underline{2B_{1u}} + \underline{2B_{2u}} + \underline{2B_{3u}}$$

$$\Gamma_D\nu(C—H)Al = A_g + B_{3g} + \underline{B_{1u}} + \underline{B_{2u}}$$

The bands which we assign to the out-of-plane C—H deformations are quite broad and therefore too much emphasis cannot be laid on the number of bands expected and observed. The spectra can be further discussed on the basis of the conclusions reached by Cannon and Sutherland (7).

Cannon and Sutherland (7) suggested that for condensed ring systems containing 3 or more rings, bands near 750 cm^{-1} arise from C—H bonds that are approximately parallel to the longer axis of the molecule, and bands near 900 cm^{-1} arise from C—H bonds approximately perpendicular to the longer axis of the molecule. 9,10-Substitution has been found (7, 11) to remove the band at 884 cm^{-1} in anthracene. Therefore the band at 884 cm^{-1} has been attributed to the deformation vibration of the C—H bonds in the 9 and 10 positions.

In the dianthracene spectrum we do not find any band near 900 cm^{-1}. This is in line with the fact that the C—H bonds at 9,10 positions are no more aromatic. On the other hand we see a new band at 810 cm^{-1}. The 727 cm^{-1} band of anthracene also shifts to higher frequencies. The band at ~810 cm^{-1} is probably due to the aliphatic C—H out-of-plane bending vibrations. The aromatic C—H bonds of dianthracene resemble ortho disubstituted benzene C—H bonds. It is interesting to note that the C—H out-of-plane bending vibrations in ortho disubstituted benzenes have been found (11) to lie in the range 740 to 760 cm^{-1} which is certainly higher than the anthracene C—H out-of-plane deformation vibration under consideration; this explains the shift of the 727 cm^{-1} band of anthracene to higher frequencies on dimerization.

TABLE II

Infrared spectra of
benzo[a]anthracene,
monomer and dimer

Position of bands	
Monomer	Dimer
3045 m	3044 s
3030 msh	3024 s
3000 w	2958 m
	2923 m
	1949 w
1910 w	1919 w
	1905 w
	1830 vw
	1800 vw
1770 wb	
1617 w	1618 m
1604 wsh	1600 vw
1580 vw	1590 msh
1560 vw	1587 m
1540 vw	1570 m
	1513 m
1447 m	1485 s
1474 m	1457 s
1450 vw	
1420 w	
1410 w	
	1385 s
1337	1370 msh
	1353 m
	1317 m
1299 m	1298 m
1290 msh	1265 m
1276 w	1243 m
1255 vw	1215 m
1238 m	1200 msh
1224 m	
1215 wsh	

TABLE II (*Concluded*)

Position of bands	
Monomer	Dimer
1170 w	1177 w
1150 w	1165 s
1135 w	1153 m
1127 w	1137 w
	1108 w
1090 w	1094 m
1037 m	1050 vw
1004 m	1034 m
	1025 m
954 m	976 m
944 m	958 m
	940 w
	936 m
	920 w
899 s	885 vw
884 vs	863 s
	842 s
844 m	830 s
811 vs	812 ssh
782 s	787 s
742 b,vs	780 m
	773 m
	760 vs
	744 vs,b
687 s	698 msh
646 w	680 msh
618 w	674 s
	644 m
	625 s
586 m	580 s
546 m	558 m
530 w	543 m
513 m	532 m
	503 m
472 s	477 w
423 m	449 m
	431 m
	422 m
	405 w

Infrared spectra of di(benzo[a]anthracene) and ditetracene are shown in Figs. 3 and 4 and the positions and relative intensities of the bands observed for the monomers and dimers have been listed in Tables II and III. Both di(benzo[a]-anthracene) and ditetracene are found to have bands below 3000 cm^{-1} due to the above discussed aliphatic C—H stretching vibrations. This shows that the mode of linkage in the three dimers under investigation is similar. The formation of aliphatic C—H bonds is a result of dimerization. Anthracene and benzo[a]anthracene on dimerization can have only 4 aliphatic C—H bonds (Fig. 5a, 5b). Ditetracene can have 4 or 8 depending on whether covalent linkage takes place at 2 centers of each tetracene molecule (Fig. 5c(i)) or 4 (Fig. 5c(ii)).

TABLE III

Infrared spectra of tetracene
monomer and dimer

| Position of bands	
Monomer	Dimer
3042 m	3060 m
3020 msh	3036 m,sh
	3010 m,sh
	2996 m,sh
	2936 w
	2915 m
1803 m	1900 wb
1737 w	1730 wb
1670 m	1580 wb
1624 m	
1534 m	
	1498 m,sh
	1496 m
	1490 w
1462 m	1477 m
	1470 m,sh
	1465 w
	1457 m
	1450 m,sh
	1430 m,sh
1386 m	1351 m
	1310 m
1295 s	
1289 s	1280 w
1270 m,sh	1266 w
	1253 w
	1212 wb
	1180 vw
1162 m	1160 vw
1122 m	1135 vw
	1100 w
	1031 m
	1018 m
995 m	976 w,b
957 s	955 m
929 w	950 m
900 vs	942 m
	888 sb
870 msh	826 w
792 vw	802 w
750 s	764 m,sh
738 vs	757 m,sh
	740 sb
	690 s
	680 m
625 m	625 w
607 m	606 s
575 w	540 s
558 w	508 w
	486 s
470 s	474 s
455 s	459 m
	419 w
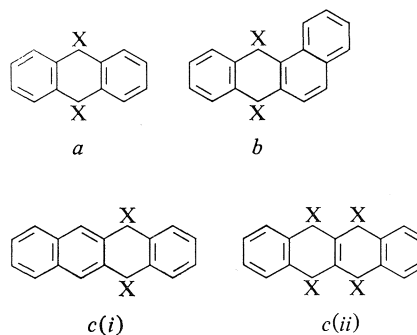
FIG. 5. Possible centers of covalent linkage in (a) anthracene, (b) benzo[a]anthracene, (c) tetracene for photodimerization.

Group theory demands 3 bands in the infrared due to aliphatic C—H stretching vibrations

$$\Gamma v(\text{C—H})\text{Al} = A_g + B_{1g} + B_{2g} + B_{3g} + A_u \\ + \underline{B_{1u}} + \underline{B_{2u}} + \underline{B_{3u}}$$

if the dimer formation is through covalent linkages at 4 centers of each tetracene molecule and D_{2h} symmetry is assumed for the dimer. On the other hand if the dimerization takes place through linkages at 2 centers only, it can have either cis (C_{2v}) or trans (C_{2h}) configuration. Three out of 4 aliphatic C—H stretching vibrations are expected to be infrared active in the cis form $(\underline{A_1} + A_2 + \underline{B_1} + \underline{B_2})$ and 2 aliphatic stretching vibrations are expected to be infrared active in the trans form $(A_g + B_g + \underline{A_u} + \underline{B_u})$. Two bands appearing at 2936 and 2915 cm^{-1} can be assigned to the aliphatic C—H stretching vibrations; this makes the trans (C_{2h}) structure more probable than the other two structures of ditetracene.

The lower frequency part of the spectrum of di(benzo[a]anthracene) is quite complicated whereas that of ditetracene is comparatively simple. Tetracene has 2 strong bands at ~900 and 750 cm^{-1} which have been assigned to C—H deformation vibrations by Cannon and Sutherland (7). A strong broad band has been found in the spectrum of ditetracene at 888 cm^{-1}. Another strong band appears at 740 cm^{-1} with shoulders at 757 and 764 cm^{-1}. Two weak bands are observed at 802 and 826 cm^{-1}. It is not possible to draw any conclusion concerning the structure of ditetracene from this part of the spectrum, but the appearance of a band at 888 cm^{-1} seems to

suggest that there are aromatic C—H bonds at axes perpendicular to the longer axis of tetracene. This is in favor of the view that covalent links are formed at 2 centers of the tetracene monomers and not 4 as suggested in Fig. 5c(ii). We cannot go further without an X-ray analysis. All the spectral conclusions are confined to the spectra in solid phase because the compounds are not soluble in solvents commonly used for recording the infrared spectra in solution. But this is expected to have only a slight influence on the spectra. Raman spectra might give additional credence to the arguments.

Acknowledgment

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