

## Electronic and Vibrational States of Tetracene (Naphthacene)\*

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The absorption and fluorescence spectra of tetracene have been studied in substitutional solid solutions in naphthalene and in anthracene at 20°K. In agreement with theoretical predictions, the lowest excited singlet state at 20 246  $\text{cm}^{-1}$  is  ${}^1B_{2u}$ ,  ${}^1L_a$ , since the transition with the ground state is polarized along the short molecular axis. Vibrational frequencies of tetracene are compared in ground and excited electronic states, and are compared with the vibrations of anthracene and naphthalene.

## I. INTRODUCTION

THE absorption and fluorescence spectra of naphthalene,<sup>1</sup> azulene,<sup>2</sup> and anthracene<sup>3</sup> have been studied in substitutional solid solutions at 20°K. Using this technique, it has been possible to determine unambiguously the symmetry properties of the excited electronic states and to measure vibrational frequencies in both ground and excited electronic states. In this paper, the same method is applied to tetracene, and the electronic and vibrational states of naphthalene, anthracene, and tetracene are compared.

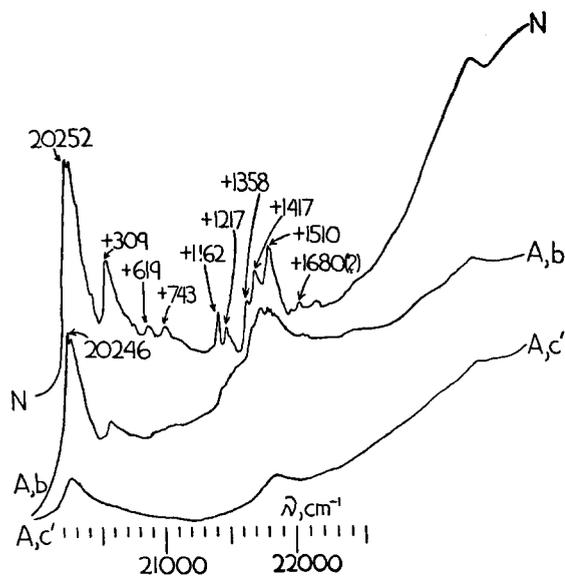


FIG. 1. Absorption spectrum of tetracene. *N*: in naphthalene, 20°K, tungsten source; *A, b*: in anthracene, *b*-axis of *bc'*-plane, 20°K, tungsten source; *A, c'*: in anthracene, *c'*-axis of *bc'*-plane, 20°K, tungsten source. The slope is due to a decrease in the source intensity at higher frequencies.

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<sup>1</sup> Donald S. McClure, *J. Chem. Phys.* **22**, 1668 (1954).

<sup>2</sup> J. W. Sidman and D. S. McClure, *J. Chem. Phys.* **24**, 757 (1956).

<sup>3</sup> J. W. Sidman, *J. Chem. Phys.* **25**, 115 (1956), preceding paper.

## II. EXPERIMENTAL

Eastman Kodak White Label tetracene was used without further purification. The technique of preparing single crystals of the dilute solid solutions has been previously described.<sup>1</sup> Using this technique, it was possible to obtain single crystals of anthracene containing approximately 0.2% of added tetracene. The absorption and fluorescence spectra of tetracene were examined in the *bc'*-face of an anthracene crystal of approximately 0.3 mm thickness. Attempts to grow solid solutions of tetracene in naphthalene did not result in a uniformly colored crystal. Some sections of the crystallized melt contained the tetracene in solid solution in naphthalene, whereas other sections contained virtually no tetracene and did not exhibit the green tetracene fluorescence when illuminated with  $\lambda 3130$  A Hg light. The segregation of tetracene in naphthalene is probably owing to the lower solubility of tetracene in naphthalene. Clear yellow sections containing tetracene in solid solution in naphthalene were used in these experiments, but single crystals could not be obtained.

Other details of apparatus and measurements have been discussed in previous papers.<sup>1-3</sup>

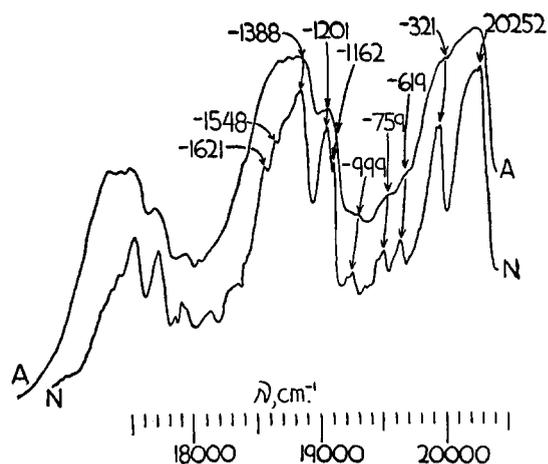


FIG. 2. Fluorescence spectrum of tetracene. *A*: in anthracene, 20°K; *N*: in naphthalene, 20°K.

TABLE I. Vibrational analysis of the absorption spectrum of tetracene in anthracene,  $bc'$ -plane, 20°K.<sup>a</sup>

Int.	$\nu$ cm <sup>-1</sup>	$\nu$ -20246	Assignment
vs	20 246	0	${}^1B_{2u} \leftarrow {}^1A_g$
s, l	20 285	39	39, lattice
m, l	20 327	81	2(39)
m	20 567	321	321, $a_g$
w, l	20 606	360	321+39
w	21 402	1156	1156, $a_g$
m	21 615	1369	1369, $a_g$
w	21 755	1509	1509, $a_g$

<sup>a</sup> v = very, s = strong, m = medium, w = weak, l = lattice, and b = broad.

### III. RESULTS AND INTERPRETATIONS

#### A. Tetracene in Anthracene

The absorption spectrum of tetracene in the  $bc'$ -plane of anthracene is shown in Fig. 1. The absorption is

TABLE II. Vibrational analysis of the fluorescence spectrum of tetracene in anthracene  $bc'$ -plane, 20°K.

Int.	$\nu$ cm <sup>-1</sup>	20246- $\nu$	Assignment
vs, broad	(20 251)	0	${}^1B_{2u} \rightarrow {}^1A_g$
vs, l	20 205	41	41, lattice
m	19 924	322	322, $a_g$
m, l	19 883	363	322+41
m	19 080	1166	1166, $a_g$
ms	19 045	1201	1201, $a_g$
m, l	18 999	1247	1201+41
s	18 851	1395	1395, $a_g$
s, l	18 806	1440	1395+41
s, broad	18 700	1546	1546, $a_g$
s, broad	18 619	1627	1627, $a_g$
m, broad	17 659	2587	1201+1395
ms, broad	17 461	2785	2(1395)

polarized along the  $b$ -axis, which corresponds to the short molecular axis in the  $bc'$ -plane.<sup>4</sup> The excited electronic state is therefore  ${}^1B_{2u}$ ,  ${}^1L_a$  if it is assumed

TABLE III. Vibrational analysis of the absorption spectrum of tetracene in naphthalene, 20°K.

Int.	$\nu$ cm <sup>-1</sup>	$\nu$ -20252	Assignment
vs	20 252	0	${}^1B_{2u} \leftarrow {}^1A_g$
vs	20 276	24	24, lattice
m, b	20 367	115	115, lattice
s	20 561	309	309, $a_g$
s	20 583	331	309+24
w, b	20 871	619	619, $a_g$
w, b	20 995	743	743, $a_g$
m, b	21 414	1162	1162, $a_g$
m, b	21 469	1217	1217, $a_g$
s	21 610	1358	1358, $a_g$
s	21 669	1417	1417, $a_g$
s	21 762	1510	1510, $a_g$
w	21 815	1563	1563, $a_g$
m	21 932	1680	1680, $a_g$
m	22 009	1757	
m	22 086	1834	
w	22 869	2617	1417+1217
w	23 213	2961	

<sup>4</sup> Sinclair, Robertson, and Mathieson, Acta Cryst. 3, 245, 251 (1950).

that the short axis of naphthalene is approximately parallel to the short axis of anthracene. The fact that the absorption spectrum is sharp and polarized indicates that all of the tetracene molecules have the same

TABLE IV. Vibrational analysis of the fluorescence spectrum of tetracene in naphthalene, 20°K.

Int.	$\nu$ cm <sup>-1</sup>	20252- $\nu$	Assignment
vvs	20 252	0	${}^1B_{2u} \rightarrow {}^1A_g$
vvs	20 233	19	19, lattice
vvs	20 212	40	2(19)
vvs	20 203	49	49, lattice
vs	20 187	65	49+19
s	20 131	121	121, lattice
s	20 076	176	121+49
w	19 954	298	
vs	19 931	321	321, $a_g$
s	19 914	338	321+19
w	19 884	368	321+49
w	19 865	387	321+49+19
m	19 809	443	321+121
m	19 762	490	321+121+49
m	19 633	619	619, $a_g$
m	19 609	643	2(321)
m	19 493	759	759, $a_g$
w	19 469	783	759+19
vww	19 448	804	759+2(19)
vww	19 430	822	759+65
vww	19 397	855	
vww	19 375	877	759+121
vww	19 274	978	
m	19 253	999	999, $a_g$
w	19 234	1018	999+19
mw	19 171	1081	759+321
mw	19 153	1099	759+321+19
s	19 090	1162	1162, $a_g$
m	19 071	1181	1162+19
vs	19 051	1201	1201, $a_g$
m	19 031	1221	1201+19
vww	18 959	1293	
w	18 929	1323	999+321
w	18 881	1371	759+619
vvs	18 864	1388	1388, $a_g$
vvs	18 843	1409	1388+19
s	18 801	1451	1388+19+49
m	18 747	1505	1388+121
m	18 732	1520	1201+321
vs	18 704	1548	1548, $a_g$
w	18 684	1568	1548+19
m	18 631	1621	1621, $a_g$
w	18 612	1640	1621+19
m	18 537	1715	1388+321
w	18 381	1871	1548+321
w	18 309	1943	1621+321
w	18 293	1959	1621+321+19
w	18 100	2152	1388+759
w	18 082	2170	1162+999
w	17 890	2362	1162+1201
w	17 858	2394	
w	17 839	2413	
m	17 705	2547	1162+1388
s	17 660	2592	1201+1388
s	17 643	2609	1201+1388+19
w	17 602	2650	
w	17 540	2712	1162+1548
w	17 503	2749	1201+1548
s	17 476	2776	2(1388)
s	17 455	2797	2(1388)+19
m	17 410	2842	2(1388)+19+49
m	17 313	2939	1388+1548
w	17 295	2957	1388+1548+19
m	17 256	2996	1388+1621
w	17 082	3170	1548+1621
w, broad	<15 800	...	...

TABLE V. Vibrational assignments for tetracene, anthracene, and naphthalene.

Tetracene		Anthracene <sup>a</sup>			Naphthalene			Assignment	
In <sup>1</sup> A <sub>g</sub> (Fluor.)	In <sup>1</sup> B <sub>2u</sub> (Abs.)	In <sup>1</sup> A <sub>g</sub> (Fluor.)	In <sup>1</sup> A <sub>g</sub> (R)	In <sup>1</sup> B <sub>2u</sub> (Abs.)	In <sup>1</sup> A <sub>g</sub> <sup>a</sup> (Fluor.)	In <sup>1</sup> B <sub>2u</sub> <sup>a</sup> (Abs.)	In <sup>1</sup> B <sub>2u</sub> <sup>c</sup> (Abs.)		
321, vs	309, s	403, vs	388(1)	399, s	509, vs	511, ν <sub>9</sub>	500, s	485	Skeletal distortion, a <sub>g</sub>
619, m	619, w								Skeletal distortion, a <sub>g</sub>
759, m	743, w	752, w	751( $\frac{1}{2}$ )		761, vs	760, ν <sub>8</sub>	702, s	710	Skeletal distortion, a <sub>g</sub>
					938, s	943, ν <sub>7</sub>	987, s	995	CH bending, a <sub>g</sub>
999, m		1003, vw	1007( $\frac{1}{2}$ )		1024, m	1024, ν <sub>6</sub>			Skeletal breathing, a <sub>g</sub>
1162, s	1162, m	1165, s	1161( $\frac{1}{2}$ )	1164, m					Skeletal breathing and CH bending, a <sub>g</sub>
1201, vs	1217, m	1264, s	1262(1)			1240, ν <sub>5</sub>	1145, m		Skeletal breathing and CH bending, a <sub>g</sub>
1388, vs	1358, s	1416, vs	1400(8)	1401, vs	1380, vs	1379, ν <sub>4</sub>	1386, vs	1390	Gamma C—C stretching, a <sub>g</sub>
1548, s	1510, s	1567, vs	1558( $3\frac{1}{2}$ )			1576, ν <sub>3</sub>	1429, vs	1520	Skeletal C—C stretching, a <sub>g</sub>
1621, m	1563 or 1680, w	1645, s	1631(3)						Skeletal C—C stretching, a <sub>g</sub>

<sup>a</sup> See reference 1.

<sup>b</sup> See reference 8. R = Raman spectral bands.

<sup>c</sup> H. Spomer and C. D. Cooper, J. Chem. Phys. 23, 646 (1955).

environment. It is therefore reasonable to assume that they fit into the anthracene lattice in the same way as the anthracene molecules. The first excited singlet state of tetracene has been previously predicted to be <sup>1</sup>B<sub>2u</sub>, <sup>1</sup>L<sub>a</sub>,<sup>5,6</sup> and the results of this investigation therefore confirm the theoretical predictions.

The fluorescence spectrum of tetracene was obtained by exciting the anthracene with λ3130 Å Hg. Previous workers<sup>7</sup> have observed polarization of the fluorescence of tetracene in the *ab*-plane of anthracene at 300°K. In this work, polarization of the fluorescence of tetracene has been observed in both the *ab*- and *bc'*-plane of anthracene at 300°K. However, the fluorescence is depolarized at 20°K. This unexpected result has also been obtained for solid solutions of anthracene in phenanthrene.<sup>3</sup> The absorption and fluorescence spectra are shown in Figs. 1 and 2 in microphotometer tracings, and vibrational analyses of the absorption and fluorescence spectra are given in Tables I and II.

### B. Tetracene in Naphthalene

The absorption and fluorescence spectra of tetracene in naphthalene at 20°K are considerably sharper than the corresponding spectra of tetracene in anthracene. Owing to the higher resolution, many vibrational intervals which are not clearly resolved in the anthracene solution are easily resolved in the naphthalene solution. The spectra are very similar except for the difference in sharpness. The O—O line is shifted only 6 cm<sup>-1</sup> to higher energies, and vibrational frequencies do not change by more than 10 cm<sup>-1</sup>. The absorption and fluorescence spectra are shown in Figs. 1 and 2, and vibrational analyses are given in Tables III and IV.

<sup>5</sup> H. B. Klevens and J. R. Platt, J. Chem. Phys. 17, 470 (1949).

<sup>6</sup> R. Pariser, talk at the Ohio State Symposium on Molecular Structure and Spectra (June 1954); J. Chem. Phys. 24, 250 (1956).

<sup>7</sup> K. S. Krishnan and P. K. Seshan, Acta Phys. Polon. 5, 289 (1936).

### C. Vibrational Frequencies and Assignments

Assignments of the vibrational frequencies of tetracene are given in Table V, and a comparison is made with the vibrational frequencies of anthracene and naphthalene. The a<sub>g</sub> vibrational frequencies of tetracene which appear in the absorption and fluorescence spectra are very similar in energy and relative intensity to the vibrations of anthracene. Since the lowest transition is <sup>1</sup>L<sub>a</sub>—<sup>1</sup>A in both anthracene and tetracene, it is not surprising to find a close correspondence in prominent vibrations. The lowest transition in naphthalene is <sup>1</sup>L<sub>b</sub>—<sup>1</sup>A. The 1578 cm<sup>-1</sup> skeletal CC stretching motion, ν<sub>3</sub>, does not appear in the fluorescence of naphthalene in durene. A frequency of 1429 cm<sup>-1</sup> does appear in absorption, and this may correspond to ν<sub>3</sub> in the <sup>1</sup>L<sub>b</sub> state of naphthalene. Skeletal CC stretching motions appear prominently in the <sup>1</sup>L<sub>a</sub>—<sup>1</sup>A transitions of anthracene and tetracene. A skeletal distortion of 761 cm<sup>-1</sup>, ν<sub>8</sub>, is quite prominent in the <sup>1</sup>L<sub>b</sub>—<sup>1</sup>A fluorescence of naphthalene in durene, but the related motion is much less prominent in the <sup>1</sup>L<sub>a</sub>—<sup>1</sup>A fluorescence of anthracene and tetracene. All spectra show the gamma (C—C) stretching, ν<sub>4</sub> (naphthalene notation),<sup>8</sup> and the skeletal distortion, ν<sub>9</sub>. The latter vibration appears to decrease in a regular manner in going from naphthalene (511 cm<sup>-1</sup>) to anthracene (403 cm<sup>-1</sup>) to tetracene (321 cm<sup>-1</sup>). This motion is related to one of the components of the degenerate 606 cm<sup>-1</sup> e<sub>g</sub><sup>+</sup> vibration of benzene.<sup>9</sup>

It is thus seen that the study of the absorption and fluorescence spectra of mixed crystals under conditions of high resolution provides a very useful adjunct to infrared and Raman spectroscopy in determining vibrational frequencies of complex molecules.

<sup>8</sup> E. R. Lippincott and E. J. O'Reilly, J. Chem. Phys. 23, 238 (1955). See also, A. McClellan and G. C. Pimentel, J. Chem. Phys. 23, 245 (1955).

<sup>9</sup> H. Spomer and E. Teller, Revs. Modern Phys. 13, 75 (1941).