but it is now seen that nickel(II) forms a stronger complex with 1,10-phenanthroline than does iron(II).

Acknowledgments.—The authors wish to thank Mr. Donn W. Klingman for his technical assistance. We should also like to express our appreciation to Dr. G. S. Hammond for his interest and criticisms.

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Electronic and Vibrational States of the Pleiadienes[1]

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RECEIVED MARCH 9, 1956

The electronic spectra of acepleiadiene and acepleiadylene have been studied in rigid glassy solution at 77°K., in dilute single mixed crystals with pyrene at 77°K. and at 4°K., and in single crystals at 77°K. The electronic transitions are assigned, using both the symmetry and the semi-empirical (Platt) classifications. Comparisons with theory indicate that the LCAO–MO, FEMO and cyclic polyene (Moffitt) perturbation theories are in good agreement with the observed results. Aromaticity in peri-condensed systems is discussed, and possible extensions of the Hückel rule are suggested. Vibrational analyses and assignments are given for the lowest absorption and fluorescence transitions in acepleiadylene and for the lowest absorption transition in acepleiadiene. A 1890 cm.$^{-1}$ crystal splitting which is observed for the lowest absorption transition in acepleiadylene is interpreted on the basis of the Frenkel–Davydov exciton theory. The lowest absorption transition of acepleiadiene shows evidence of crystal-induced mixing of molecular transitions. The crystal spectra give information regarding some of the gross features of the crystal structure.

Introduction

The lower electronic transitions of numerous cata-condensed hydrocarbons have been studied by D. S. McClure and co-workers, using single crystals and mixed crystals in polarized light at low temperatures.[3] These studies have provided detailed information about the polarization properties and vibrational structure of the transitions, and have clarified earlier discrepancies concerning symmetry assignments of the electronic transitions. Furthermore, from a comparison of the spectra of the ordinary and mixed crystals, it has been possible to arrive at conclusions concerning the nature of the intermolecular forces and their effects on the spectra of molecular crystals.[4]

Recently, Boekelheide and co-workers have reported the synthesis of acepleiadiene,[5a] pleiadiene and acepleiadylene.[5b] In addition to their intrinsic interest, these peri-condensed hydrocarbons containing five- and seven-membered rings provide a proving ground for the theories of molecular structure which have been developed primarily for the cata-condensed hydrocarbons. In this paper, the results of the spectral studies of the lower electronic transitions of these molecules are reported. The results are compared with the predictions of previous theories, and additional predictions are made. Finally, the study of the crystal spectra is used to provide some information about the structure of the crystal.

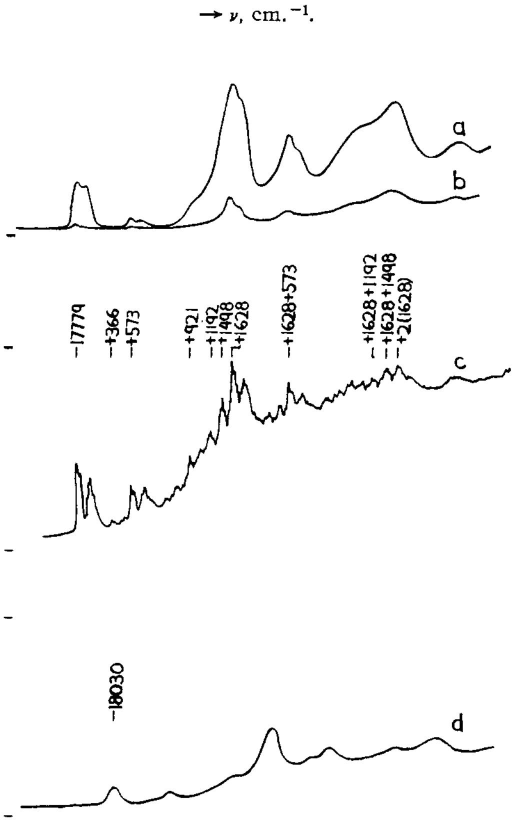

Fig. 1.—The $^1L_b \leftarrow {}^1A$ absorption transition of acepleiadylene: (a) single mixed crystal with pyrene, 77°K. for light polarized along the *a*-axis in the *ab* face; (b) same as (a), but for light polarized along the *b*-axis; (c) mixed crystal with pyrene, 4°K.; (d) rigid glass, 77°K.

Experimental

The spectrograph used in this research was a Bausch and Lomb quartz prism Littrow spectrograph. The experimental arrangement used to record the spectra was similar to one which has been previously described.[6] The rigid

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[1] This research was supported by the Office of Ordnance Research, under contract DA-30-115-Ord 620 with the University of Rochester. Presented at the Symposium on Molecular Spectra and Structure at the Ohio State University, Columbus, Ohio, in June, 1956.

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[3] See, for example, naphthalene in durene: D. S. McClure, *J. Chem. Phys.*, **22**, 1668 (1954).

[4] (a) D. S. McClure and O. Schnepp, *ibid.*, **23**, 1575 (1955); (b) J. W. Sidman, *Phys. Rev.*, **102**, 96 (1956).

[5] (a) V. Boekelheide, W. E. Langeland and C. T. Liu, THIS JOURNAL, **73**, 2432 (1951); (b) V. Boekelheide and G. K. Vick, *ibid.*, **78**, 653 (1956).

[6] J. W. Sidman and D. S. McClure, *ibid.*, **77**, 6461, 6471 (1955).

glass spectra were obtained at 77°K. in a glass consisting of four volumes of CH_3OH to one volume of C_2H_5OH. The mixed crystals were prepared by fusing acepleiadiene or acepleiadylene with pyrene. Microscopic examination revealed that only one phase separated when a melt between quartz plates was allowed to solidify. Clear, light reddish-pink single crystals containing less than 0.5% of the red hydrocarbon could easily be prepared by this technique. Their spectra were recorded at 77°K. and at 4°K., with the sample immersed directly in the appropriate liquid refrigerant (77°K., liquid nitrogen; 4°K., liquid helium). The spectra of the crystals were obtained in a similar manner. A Wollaston prism was used in conjunction with spectral studies of single crystals and single mixed crystals in polarized light. The spectra were photographed on Kodak 103-F plates, and the wave lengths were determined from a Hartmann dispersion formula which reproduced the wave lengths of the iron arc calibration lines to better than 0.3 Å. A tungsten lamp was used as a light source in the absorption experiments, and a medium-pressure Hg arc with appropriate filters was used to excite fluorescence.

Results

The bands which are observed in the lowest absorption transition of acepleiadylene in pyrene at 4°K. are listed in Table I. The corresponding fluorescence bands due to acepleiadylene in pyrene at 4°K. are listed in Table III. The vibrational analyses which accompany the tables will be discussed later. The absorption and fluorescence spectra of these hydrocarbons are shown in Figs. 1, 2 and 3.

TABLE I

ANALYSIS OF THE $^1L_b \leftarrow {}^1A$ ABSORPTION TRANSITION OF ACEPLEIADYLENE IN PYRENE, 4°K.

Intensity	ν, cm.$^{-1}$ ±4	ν-17779	Assignment
vvs	17779	0	0–0, $^1L_b \leftarrow {}^1A$, $^1A_1 \leftarrow {}^1A_1$
vs	17795	16	16, lattice
s	17806	27	27, lattice
s	17821	42	27 + 16
s	17881	102	102, lattice
vs	17903	124	124, lattice
vs	17927	148	124 + 16
s	17954	175	124 + 27 + 16
w	18145	366	366, a_1
vw	18288	509	509, a_1(?)
s	18352	573	573, a_1
s	18368	589	573 + 16
m	18390	611	573 + 16 + 27
m	18462	683	573 + 102
m	18468	707	573 + 124
m	18509	730	2(366)
w	18700	921	921, a_1(?)
w	18718	939	921 + 16; 573 + 366
w	18804	1025	
w	18824	1045	
w	18850	1071	
m	18917	1138	2(573)
ms	18971	1192	1192, a_1
m	19037	1258	
m	19070	1291	1192 + 102
m	19152	1373	
m	19176	1397	
m	19200	1421	
s	19277	1498	1498, a_1
s	19301	1522	1498 + 27
s	19327	1548	1192 + 366
vs	19407	1628	1628, a_1
vs	19431	1652	1628 + 27
s	19458	1679	1628 + 27 + 16
s	19497	1718	1628 + 102
s	19524	1745	1628 + 124
s	19555	1776	1628 + 124 + 27
m	19584	1805	1628 + 124 + 2(27)
w	19647	1868	1498 + 366
w	19679	1900	
w	19753	1974	
w	19787	2008	
w	19855	2076	1498 + 573
w	19892	2113	
s	19978	2199	1628 + 573
ms	20011	2232	1628 + 573 + 27
m	20061	2282	
w	20092	2313	1628 + 573 + 102
w	20114	2335	1628 + 573 + 124
w	20189	2410	
w	20215	2436	
w	20330	2551	1628 + 921
w	20360	2581	1628 + 921 + 27
w	20445	2666	
w	20468	2689	1498 + 1192
m	20583	2804	
m	20607	2828	1628 + 1192
m	20680	2901	
m	20700	2921	
m	20773	2994	2(1498)
m	20795	3016	2(1498) + 27
s	20910	3131	1628 + 1498
s	20937	3158	1628 + 1498 + 27
s	21027	3248	2(1628)
s	21053	3274	2(1628) + 27
m	21154	3375	2(1628) + 124
m	21184	3405	2(1628) + 124 + 27
w	21271	3492	1628 + 1498 + 366
w	21296	3517	
w	21378	3599	
w	21394	3615	
m	21480	3710	1628 + 1498 + 573
m	21499	3720	1628 + 1498 + 573 + 16
m	21604	3825	2(1628) + 573
m	21630	3851	
w	>21700		

TABLE II

ANALYSIS OF THE $^1L_b \rightarrow {}^1A$ FLUORESCENCE TRANSITION OF ACEPLEIADYLENE IN PYRENE, 4°K.

Intensity	ν, cm.$^{-1}$, ±6	17779-ν	Assignment
(vvs, reabsorbed)	17779	0	0–0. $^1L_b \rightarrow {}^1A$, $^1A_1 \rightarrow {}^1A_1$
vs	17751	28	28, lattice
s	17725	54	2(28)
m	17409	370	370,a_1
m	17266	513	513,a_1
vs	17184	595	595,a_1
w	17066	713	
w	16776	1003	
s	16695	1084	1084,a_1
m	16587	1192	1192,a_1
vs	16380	1399	1399,a_1
m	16268	1511	1511,a_1
m	16107	1672	1084 + 595
m	15772	2007	1399 + 595
m	15309	2470	1399 + 1084
m	15234	2545	
m	14970	2809	2(1399)
(limit of plate sensitivity)	<14500		

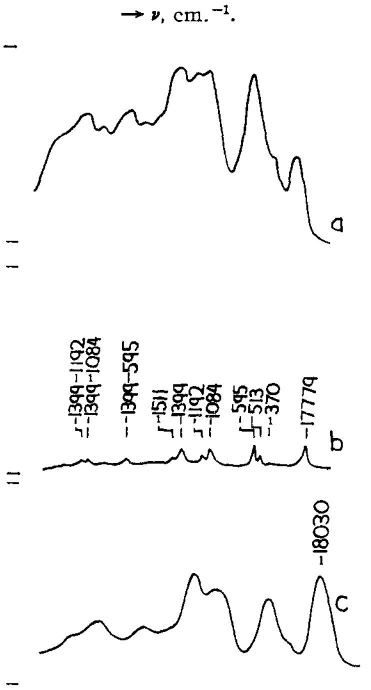

Fig. 2.—The $^1L_b \rightarrow {}^1A$ fluorescence transition of acepleiadylene: (a) mixed crystal with pyrene, 77°K.; (b) mixed crystal with pyrene, 4°K.; (c) rigid glass, 77°K.

Discussion

Previous experience with the cata-condensed hydrocarbons has revealed that the mixed crystal spectra are usually the simplest to interpret. The crystal spectra often show peculiarities which can be understood only after the molecular transition in the mixed crystal has been analyzed. For many purposes, the spectrum of the dilute mixed crystal closely approximates an oriented gas in a regular medium of high local electric field. The mixed crystal spectra may be shifted (usually to lower frequencies) with respect to the vapor spectra,[3] and degenerate transitions may be split if the symmetry of the environment is lower than the symmetry of the free molecule.[7,8] However, the polarization properties of the absorption transitions in the mixed crystal have been shown to be characteristic of the transition in the isolated molecule, and vibrational-electronic interaction in the mixed crystal spectra has been interpreted in terms of intramolecular perturbations in the isolated molecule.[3] Consequently, the mixed crystal spectra will be discussed first, since they lead to an intimate understanding of the nature of the molecular transition. The crystal spectra often show additional complexities, such as dichroic (Davydov) splitting,[4a] crystal-induced mixing of different molecular transitions,[4a] and "trapped exciton" states.[4b] A comparison of crystal and mixed crystal spectra aids in revealing the complexities which are due to the crystal, since these are absent in the spectra of the dilute mixed crystals.

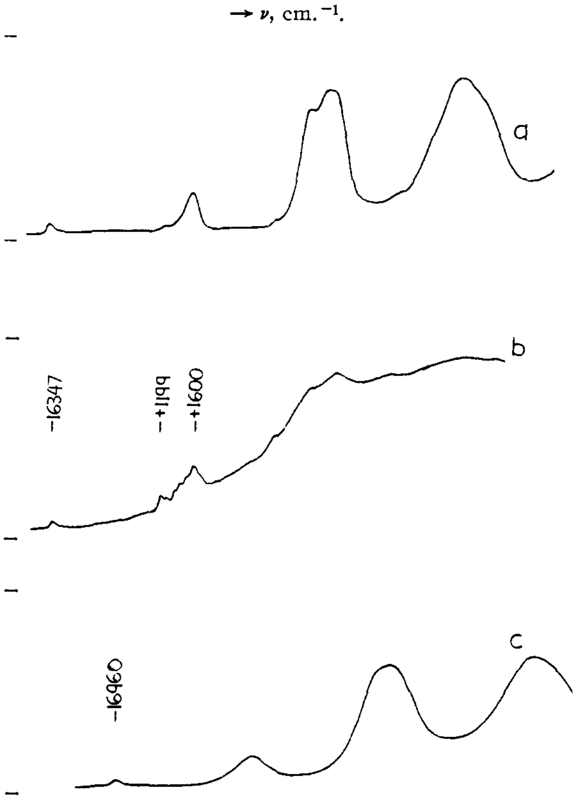

Fig. 3.—The $^1L_b \leftarrow {}^1A$ absorption transition of acepleiadiene: (a) single mixed crystal with pyrene, 77°K., for light polarized along either the *a*- or the *b*-axis in the *ab* face; (b) mixed crystal with pyrene, 4°K.; (c) rigid glass, 77°K.

A. Assignments of the Electronic Transitions. (1) Experimental.—The crystal structure of pyrene has been determined by Robertson and White.[9] A microscopic examination of crystalline pyrene in polarized light revealed that the *ab* face was always the exposed face when a melt was allowed to solidify between quartz plates, and observation of the indicatrix enabled the *a*- and *b*-axes to be distinguished.[10] In the *ab* face of pyrene, the molecules are oriented in such a way that a molecular transition with an oscillating dipole along the long molecular axis would be six times as intense for light polarized along the *a*-axis as for light polarized along the *b*-axis, whereas a molecular transition with an oscillating dipole along the short molecular axis would show equal intensities for both *a*- and *b*-axis polarizations. These values are computed by finding the square of the projection of each molecular axis on each crystal axis. Since additional information is lacking, one is forced to assume that the acepleiadiene and acepleiadylene will enter the pyrene lattice in the manner which least alters the crystal structure. This will occur only if the symmetry axis is approximately parallel to the long axis of the pyrene molecule, and if the transverse direction is approximately parallel to the short axis of the pyrene molecule. In dilute single mixed crystals of acepleiadiene with pyrene, the lowest absorption transition shows no variation of intensity with direction of polarization when viewed with

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[7] For the very interesting case of MnO_4^-, see: J. Teltow, *Z. physik. Chem.*, **B40**, 397 (1938); **B43**, 198 (1939).

[8] Also, M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

[9] J. M. Robertson and J. G. White, *J. Chem. Soc.*, 358 (1947).

[10] P. Groth, *Chem. Kryst.*, **5**, 437 (1919).

polarized light in the *ab* face. Under the same conditions, dilute single mixed crystals of acepleiadylene in pyrene show a much stronger absorption for light polarized along the *a*-axis than for light polarized along the *b*-axis. Microphotometer tracings of the polarized absorption spectra are shown in Figs. 1 and 3 for acepleiadylene and acepleiadiene, respectively. These results are consistent only with a molecular transition which is transversally polarized in acepleiadiene and polarized along the symmetry axis in acepleiadylene.[11] Assuming a totally symmetric ground state in each case, the group-theoretical symmetry assignments are then $^1B_1 \leftarrow {}^1A_1$ for acepleiadiene, and $^1A_1 \leftarrow {}^1A_1$ for acepleiadylene. Neither transition appears to possess any component of the opposite polarization, since the polarization of the vibrational structure remains the same throughout each transition.

2. Theoretical.—In addition to a classification based on symmetry, a classification based on spectral resemblances has been found to be useful. Platt[12] has developed a classification of the spectra of cata-condensed aromatic hydrocarbons which is based on spectral resemblances shown by many aromatic hydrocarbons. The method of the polarization diagram[12] has been used by Platt to predict symmetry properties of the $\pi \rightarrow \pi^*$ transitions in the aromatic hydrocarbons. Recent experimental work using mixed crystals has verified Platt's predictions for the lower electronic transitions in naphthalene,[1] azulene,[13] anthracene[14] and tetracene.[15]

In view of the success of Platt's classification scheme in treating the spectra of the cata-condensed hydrocarbons, it would appear desirable to attempt to extend this scheme to peri-condensed hydrocarbons.[16] In a later paper, Platt has considered the free-electron box model and electron densities in conjugated systems.[17] This paper stresses the periodic table of convex conjugated hydrocarbons which results from a free-electron box potential and the Pauli principle. In a peri-condensed hydrocarbon molecule such as pyrene or acepleiadylene, the free-electron model gives rise to sets of orbitals differing in the number of radial nodes, analogous to the K, L, etc., "shells" of an atom. As a first approximation, the lowest $\pi \rightarrow \pi^*$ transitions involve only the orbitals of the outermost perimeter, which are higher in energy than the orbitals of the inner perimeter. Applying the method of the polarization diagram to the outer perimeter of pyrene and acepleiadylene, it is seen that a $^1L_b \leftarrow {}^1A$ transition is polarized along the transverse (short) axis in pyrene and along the symmetry (long) axis in acepleiadylene.[18] The polarization diagram cannot be applied to pleiadiene, since the outer perimeter contains an odd number of atoms, and no prediction is possible on this basis.[19] Recent FEMO calculations by Ham and Rüdenberg[20] predict that the lowest absorption transition in pyrene is $^1L_b \leftarrow {}^1A$, with a short-axis transition moment, in agreement with Platt's earlier predictions.[17]

Pullman, *et al.*, have performed LCAO–MO calculations for the pleiadienes.[21] In pleiadiene, the lowest orbital transition corresponds to a $B_1 \leftarrow A_1$ electronic transition (transverse polarization) with excitation energy 0.8563 γ, whereas the next orbital transition corresponds to a $A_1 \leftarrow A_1$ transition (symmetry-axis polarization), with excitation energy 1.0895 γ. If the value γ = 23 k.cm.$^{-1}$, which was found to be moderately successful in accounting for the spectra of the cata-condensed hydrocarbons,[22] is used to calculate the mean configurational transition energy, the predicted energies are 19.6 and 25.0 k.cm.$^{-1}$, in fairly good agreement with the experimental values for the first two transitions. The symmetry properties are correct for the first transition in acepleiadiene, and, as will be shown later, are very probably also correct for the second transition. In the case of acepleiadylene, the lowest excited configuration is predicted to be A_1, 20.7 k.cm.$^{-1}$. Here again, the agreement is fairly good for the energy and excellent for the symmetry. However, there are two low excited A_1 configurations, with energies 0.9103 and 1.1381 γ, and two low excited B_1 configurations, with energies 0.9758 and 1.0736 γ. A configurational interaction therefore appears necessary for acepleiadylene, since the energies of several low excited configurations are so similar. It is perhaps fortuitous that the predicted properties of the lowest transition in acepleiadylene agree so well with the experimentally observed values.

Thus, it appears that the experimentally observed symmetry properties for the lowest transitions in acepleiadiene and acepleiadylene support the predictions of the various theories in the cases in which predictions have been made, and lead to $^1L_b \leftarrow {}^1A$ assignments for the lowest $^1B_1 \leftarrow {}^1A_1$ transition in acepleiadiene and for the lowest $^1A_1 \leftarrow {}^1A_1$ transition in acepleiadylene. The low intensity (log ϵ 2.3) in acepleiadiene is consistent with a $^1L_b \leftarrow {}^1A$ assignment. The moderate intensity (log ϵ 3.5) in acepleiadylene is rather high for a $^1L_b \leftarrow {}^1A$ transition. This may be due to the long-field nature of the π-skeleton in pyrene and in acepleiadylene, which tends to break down the angular-momentum type selection rule which is used to account for the low intensity of $^1L_b \leftarrow {}^1A$ transitions in round-field π-skeletons like naphthalene.[22]

A comparison of the electronic transitions in pyrene and acepleiadylene is shown in Fig. 4. The electronic transitions of acepleiadiene are also shown, and assignments are suggested for the vari-

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[11] J. W. Sidman, This Journal, **78**, 1261 (1956).

[12] J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949).

[13] J. W. Sidman and D. S. McClure, *ibid.*, **24**, 757 (1956).

[14] J. W. Sidman, *ibid.*, **25**, 115 (1956).

[15] J. W. Sidman, *ibid.*, **25**, 122 (1956).

[16] A cata-condensed hydrocarbon possesses no carbon atom which is common to more than two rings, whereas a peri-condensed hydrocarbon possesses one or more carbon atoms which are common to three rings.

[17] J. R. Platt, *J. Chem. Phys.*, **22**, 1448 (1954).

[18] The ^1L_b state possesses a nodal surface in the free-electron π wave function through each carbon atom on the perimeter, whereas the ^1L_a state possesses a nodal surface through each carbon–carbon bond on the perimeter.

[19] The statement in reference 11, that a prediction is possible in pleiadiene or acepleiadiene on the basis of the polarization diagram, is incorrect. I am grateful to the referee for criticisms which have pointed this out.

[20] N. S. Ham and K. Rüdenberg, *J. Chem. Phys.*, **25**, 1, 13 (1956).

[21] B. Pullman, A. Pullman, G. Berthier and J. Pontis, *J. chim. phys.*, **49**, 20 (1952).

[22] J. R. Platt, *J. Chem. Phys.*, **18**, 1168 (1950).

ous transitions. The large decrease in the energy of the $^1L_b \leftarrow {}^1A$ transition in acepleiadylene relative to pyrene is similar to the large decrease in the energy of the $^1L_b \leftarrow {}^1A$ transition in azulene relative to naphthalene, which has been accounted for by Moffitt by a simple perturbed cyclic polyene model for a cata-condensed hydrocarbon.[23] As has been previously mentioned,[11] Moffitt's perturbation theory appears to apply to peri-condensed as well as to cata-condensed hydrocarbons.

B. Aromaticity in Peri-condensed Systems.—In cata-condensed hydrocarbons, the Hückel rule[24] has been remarkably successful in predicting stability or the lack of it in a wide variety of aromatic compounds. Consequently, it would appear desirable to attempt to extend this rule to peri-condensed hydrocarbons. Strictly speaking, the rule that a hydrocarbon will possess properties associated with aromaticity if it contains $(4n + 2)$ π-electrons, where n is an integer, applies only to a cyclic polyene. Moffitt has shown that it is a good approximation to consider a cata-condensed hydrocarbon as a perturbed cyclic polyene.[17] Numerous peri-condensed aromatic hydrocarbons such as pyrene, perylene and coronene do not satisfy the Hückel rule if the total number of π-electrons are considered. If, as discussed in the previous section, these hydrocarbons are considered to be two (or more) concentric cylic polyenes in which some of the bonds connect the perimeters with each other, it is seen that each of the perimeters separately satisfies the Hückel rule. In FEMO terms,[17,20] this is described by saying that the orbitals with a different number of radial nodes do not interact appreciably, since their spatial distributions are very different, so that a separation on the basis of the number of radial nodes in the wave function leads to the picture of two (or more) concentric rings which may act more or less independently of each other if each one satisfies the $(4n + 2)$ rule.

In pleiadiene, the perimeters do not separately satisfy the Hückel rule, although their sum does. Pleiadiene therefore cannot be considered as a perturbed cyclic polyene, and the entire skeleton must be taken as the basic aromatic unit. In acenaphthylene, neither the separate perimeters nor their sum satisfies the Hückel rule, and it therefore appears best to consider it as a vinyl disubstituted naphthalene. This is in agreement with the smaller change in the ultraviolet spectrum between naphthalene and acenaphthylene[25] than between pleiadiene and naphthalene.

C. Analysis of the Vibrational Structure.—In the electronic spectrum of a large polyatomic molecule, the analysis of the vibrational structure gives insight into the change in the electronic distribution in the molecule when it undergoes a transition between two electronic states. In the cata-condensed hydrocarbons, regularities in the vibrational structure have been observed in a wide variety of molecules in ground and in excited electronic states.[15] The most prominent vibrational frequencies fall roughly into three classes.

(1) In the region from 300 to 700 cm.$^{-1}$ there is usually at least one prominent vibrational frequency. In naphthalene,[3] this is the 512 cm.$^{-1}$ skeletal bending motion, which is in turn related to one of the components of the degenerate 606 cm.$^{-1}$ vibration in benzene.

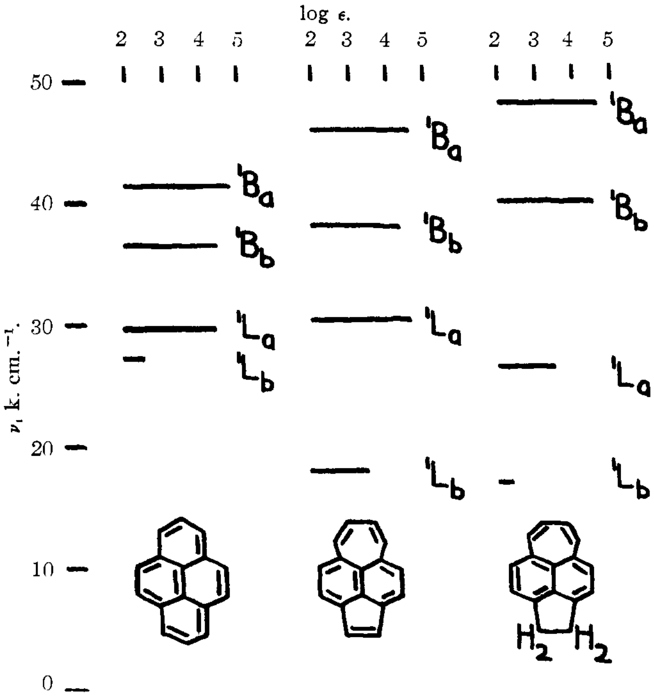

Fig. 4.—Assignments of the electronic transitions in pyrene, acepleiadylene and acepleiadiene.

(2) In the region from 800 to 1200 cm.$^{-1}$, there are usually several vibrational frequencies, which have been assigned in naphthalene[3,26,27] to motions involving skeletal breathing and CH bending.

(3) In the region from 1300 to 1600 cm.$^{-1}$, there is usually a vibrational frequency between 1380 and 1430 cm.$^{-1}$ which is the most prominent single frequency in the spectrum. In naphthalene, this frequency is 1380 cm.$^{-1}$ in the ground electronic state.[3] Since this frequency is virtually unchanged in naphthalene-d_8, it has been assigned to the stretching of the C–C bond between the rings.[26,27] There is often another prominent frequency between 1550 and 1600 cm.$^{-1}$. Although it does not appear in the fluorescence of naphthalene in durene,[3] it does appear in the phosphorescence spectra of β-halonaphthalenes in naphthalene at 20°K.[28] This frequency is 1575 cm.$^{-1}$ in naphthalene, and probably corresponds to a motion in which each carbon atom moves against its neighbors.

It is also observed that corresponding vibrational frequencies in ground and in excited states are usually not different by more than 50 cm.$^{-1}$. Except in the relatively few cases in which vibrational-

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(23) W. Moffitt, *J. Chem. Phys.*, **22**, 320 (1954).

(24) E. Hückel, *Z. Elektrochem.*, **43**, 752, 827 (1937).

(25) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951.

(26) E. R. Lippincott and E. J. O'Reilly, *J. Chem. Phys.*, **23**, 238 (1955).

(27) A. McClellan and G. C. Pimentel, *ibid.*, **23**, 245 (1955).

(28) J. W. Sidman, *ibid.*, **25**, in press (1956).

electronic interaction with non-symmetric vibrations contributes to the intensity (as in the $^1L_b \leftarrow {}^1A$, $^1B_{3u} \leftarrow {}^1A_g$ transition in naphthalene,[3] and in the $^1L_a \leftarrow {}^1A$, $^1A_1 \leftarrow {}^1A_1$ transition in azulene),[13] the vibrational frequencies which appear in the transition are best interpreted as totally symmetric vibrations.[29]

With these observations in mind, it is now profitable to consider the vibrational structure of the electronic transitions in the pleiadienes. The vibrational analyses of the acepleiadylene absorption and fluorescence transitions are given in Tables I and II. Although the spectra are complex, certain regularities are apparent. In the region of skeletal bending, three vibrational frequencies, of which the 595 cm.$^{-1}$ (573 cm.$^{-1}$ in ^1L_b) vibration is the most prominent, appear in the spectra. In the region of skeletal breathing and C–H bending, two frequencies appear in fluorescence, although only one of them (1192 cm.$^{-1}$ in ^1L_b and in ^1A) has been identified with certainty in absorption. In the region of C–C stretching two vibrations appear both in absorption and in fluorescence. It is observed that the most prominent vibration in absorption is 1628 cm.$^{-1}$ whereas the corresponding vibration in fluorescence appears to be 1399 cm.$^{-1}$. The vibrational analysis of the absorption conclusively reveals the 1628 cm.$^{-1}$ vibration, as may be seen in Table I, since it is the most important progression-forming vibration in the spectrum. The corresponding progression-forming vibration in fluorescence is the 1399 cm.$^{-1}$ vibration, so that these two vibrations appear to correspond with respect to their prominence in the spectrum, even though the frequency is higher by 129 cm.$^{-1}$ in the ^1L_b state than in the ^1A state. This sort of change has no precedent in any of the high-resolution electronic spectra of aromatic hydrocarbons which have been studied thus far. It may indicate that a considerable change has occurred in the electronic distribution in the excited state. Since 1628 cm.$^{-1}$ is in the region of C=C stretching in an isolated double bond (1623 cm.$^{-1}$ in ethylene in the ground electronic state[30]), it is possible that one particular bond has acquired in the excited state a large amount of double bond character which it does not possess in the ground state. The most likely bond is the central bond which connects the two carbon atoms in the inner perimeter. The language of the valence bond (VB) method is more suitable than the language of the molecular orbital (MO) method for discussing individual bonds. In terms of the VB description, the two Kekule structures in which the central bond is single contribute more to the ground state, whereas the two Kekule structures in which the central bond is double contribute more to the excited state. Both the ^1L_b and the ^1A states should be stabilized by aromatic resonance, since the outer perimeter has two Kekule structures in both the double and the single central bond structures.

If the interpretation which has been stated is accepted, it appears that the simple orbital theory which has been used to discuss the electronic assignments is too crude an approximation to account for the details of the vibrational structure. Although this difficulty has not appeared previously in the study of the $\pi \rightarrow \pi^*$ transition of cata-condensed aromatic hydrocarbons,[13–15] it was found that the simple orbital theory did not give a good description of the changes in vibrational frequencies in the $n \rightarrow \pi^*$ transitions of biacetyl.[6] In acepleiadylene, the appearance of a vibrational frequency corresponding to stretching of the bond between the carbon atoms on the inner perimeter is unexpected, since the lowest transitions supposedly involve the orbitals of the outer perimeter. However, it may be that the molecule in the excited state compensates for loss of bonding in the outer perimeter by an increase in bonding in the inner perimeter. The problem of the vibrational structure of electronic transitions of polyatomic molecules is a complex one, and additional studies will be needed to clarify this important point in molecules as large as the ones discussed in this work.

The vibrational analysis of the $^1L_b \leftarrow {}^1A$ transition in acepleiadiene is given in Table III. Very many vibrations appear to be excited in this transition. The value of low temperature spectral measurements is readily apparent in this case, since the solution spectra at room temperature do not resolve any of the vibrations in this region. Since so many vibrations are excited in absorption, the large number of combinations with similar energy causes the spectrum to appear almost diffuse at energies higher than 19500 cm.$^{-1}$, and the analysis then becomes impossible.

TABLE III

ANALYSIS OF THE $^1L_b \leftarrow {}^1A$ ABSORPTION TRANSITION OF ACEPLEIADIENE IN PYRENE, 4°K.

Intensity	ν, cm.$^{-1}$, ±6	ν-16347	Assignment
s	16347	0	0–0, $^1L_b \leftarrow {}^1A$, $^1B_1 \leftarrow {}^1A_1$
w	16934	587	587,a_1
vw(?)	17212	865	865,a_1(?)
vw(?)	17360	1013	1013,a_1(?)
s	17546	1199	1199,a_1
s	17581	1234	1234,a_1
s	17620	1273	1273,a_1
m	17671	1324	1324,a_1
s	17735	1388	1388,a_1
s	17784	1437	1437,a_1
vs	17856	1509	1509,a_1
vs	17947	1600	1600,a_1
m	18746	2399	2(1199)
s to w	>18800		

No fluorescence was observed when acepleiadiene was excited in rigid glassy solution, in the mixed crystal with pyrene, or in the crystalline state, using either λ 3660 Å. or λ 4358 Å. from a mercury arc. Consequently, a comparison of ground and excited state vibrational frequencies is more difficult. However, some progress can be made if the infrared spectra are examined. The infrared spectra of acepleiadylene and acepleiadiene are shown in Fig. 5.[31] In a molecule with C_{2v} symmetry, the totally symmetric (a_1) vibrations which may appear in fluorescence are also active in infrared absorption. It is possible to correlate many of the vibra-

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(29) H. Sponer and E. Teller, *Rev. Mod. Phys.*, **13**, 75 (1941).

(30) W. S. Gallaway and E. F. Barker, *J. Chem. Phys.*, **10**, 88 (1942).

(31) These spectra are taken from the Ph.D. thesis of G. K. Vick, University of Rochester, with permission of Professor V. Boekelheide.

tional frequencies of acepleiadylene which have been deduced from the vibrational analysis of the fluorescence spectrum with those which appear in the infrared absorption spectrum, as shown in Table IV. If it is assumed that most of the excited state vibrational frequencies of acepleiadiene which appear in the $^1L_b \leftarrow {}^1A$ absorption transition are not greatly different from those in the ground electronic state, it is then possible to find infrared absorption bands in the expected region. The correlation in this case, which is shown in Table V, is naturally subject to some uncertainty, since a fluorescence spectrum of acepleiadiene is lacking, but several reasonable correspondences are apparent. Partial vibrational assignments for acepleiadylene and for acepleiadiene in the ^1L_b and ^1A states are given in Tables IV and V.

TABLE IV

PARTIAL VIBRATIONAL ASSIGNMENTS FOR ACEPLEIADYLENE

In ^1L_b Anal. of absorpn. ν, cm.$^{-1}$, ±6	In ^1A Anal. of fluorescence ν, cm.$^{-1}$, ±8	Infrared absorpn. ν, cm.$^{-1}$, ±20	Assignment
366,w	370,w	Not studied	Skeletal bending, a_1
509,vw	513,m	Not studied	Skeletal bending, a_1
573,s	595,s	Not studied	Skeletal bending, a_1
(?)921,w	1084,s	1090,s	Skeletal breathing and CH bending, a_1
1192,ms	1192,m	1190,m	Skeletal breathing and CH bending, a_1
1628,vs	1399,vs	1420,s	Skeletal stretching, a_1
1498,s	1511,m		Skeletal stretching, a_1

TABLE V

PARTIAL VIBRATIONAL ASSIGNMENTS FOR ACEPLEIADIENE

In ^1L_b Anal. of absorpn. ν, cm.$^{-1}$, ±6	In ^1A Infrared absorption ν, cm.$^{-1}$, ±20	Assignment
587,w	Not studied	Skeletal bending, a_1
1199,s	1190,m	Skeletal breathing, CH and CH_2 bending,a_1
1234,s	1230,m	
1273,s	1280,m	
1324,m		Skeletal stretching, a_1
1388,s		
1437,s	1430,vs	
1509,vs		
1572,vs		
1600,vs	1600,vs	

D. The Absorption Spectra of the Pleiadienes in the Crystalline State.—The analyses of the absorption spectra of the mixed crystals of the pleiadienes with pyrene have led to rather detailed conclusions about the lower electronic states of the molecules. These conclusions will now be applied to an analysis of the absorption spectra of the pleiadienes in the crystalline state. Since the crystal structures are not yet known, the spectral interpretations will necessarily be somewhat tentative. On the other hand, an effort will be made to deduce some information about the crystal structure from an analysis of the spectrum.

The similarity in size and shape of acepleiadylene and pyrene leads to the expectation that their crystal structures are probably not very different with respect to the orientation of the molecules in the crystals. Their very close similarity in melting points is further evidence in this direction. If this assumption is made, it is possible to predict several features of the crystal spectrum, which may then be compared with experiment. It will be found that the assumption is borne out in several respects.

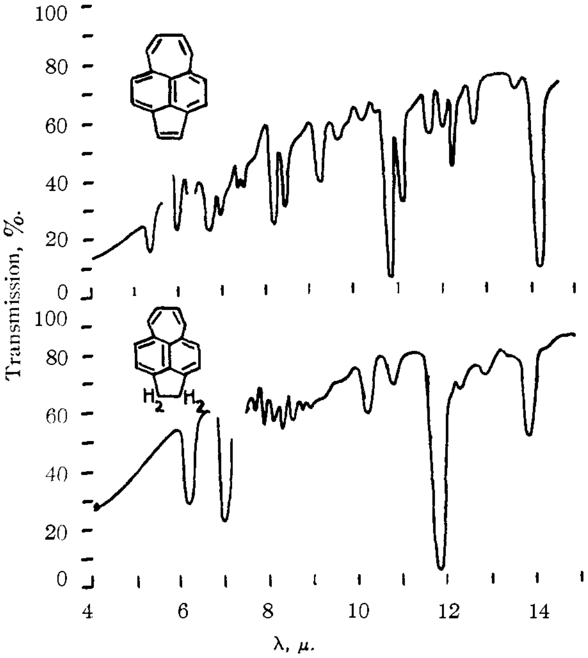

Fig. 5.—Infrared absorption spectra of acepleiadylene and acepleiadiene: Perkin-Elmer spectrophotometer, model 12-A, NaCl prism; Nujol mulls.

The $^1L_b \leftarrow {}^1A$ transition in acepleiadylene is moderately intense (log ϵ, 3.5) and is polarized along the symmetry axis ($^1A_1 \leftarrow {}^1A_1$), which corresponds to the long molecular axis in pyrene. In the pyrene crystal, the long molecular axes of the different molecules, while by no means strictly parallel, nevertheless have large projections on each other, whereas the short molecular axes are rather close to being perpendicular to each other, and have only small projections on each other.[9] In this respect, which is important in determining intensity dichroisms and dichroic (Davydov) energy splittings, the crystal structure of pyrene is similar to the structure of crystalline anthracene[32] or naphthalene.[33] In the electronic spectra of crystalline anthracene and naphthalene, considerable Davydov splittings[34] have been observed for transitions which are polarized along the long molecular axis, whereas, due to unfavorable molecular arrangements, transitions polarized along the short molecular axis show little or no crystal splitting. Thus, in crystalline anthracene, the very intense $^1B_b \leftarrow {}^1A$, $^1B_{3u} \leftarrow {}^1A_g$ transition at 39,000 cm.$^{-1}$ [35] (log ϵ 5.3) should show a dichroic splitting of approximately 16000 cm.$^{-1}$ according to calculations by Craig based on the Frenkel–Davydov free exciton

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(32) V. Sinclair, J. M. Robertson and A. M. Mathieson, *Acta Cryst.*, **3**, 245, 251 (1950).

(33) S. C. Abrahams, J. M. Robertson and J. G. White, *ibid.*, **2**, 233, 238 (1949).

(34) A. S. Davydov, *Zhur. Ekspll. Teoret. Fiz.* (*USSR*), **18**, 210 (1948).

(35) H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949).

theory.[36] Recent experimental work by Lyons has substantiated the predictions.[37] The moderately intense (log ϵ 3.8) $^1L_a \leftarrow {}^1A$, $^1B_{2u} \leftarrow {}^1A_g$ absorption system of anthracene at 27000 cm.$^{-1}$ shows little or no crystal splitting.[4b,38,39] The agreement between calculations and experiment in crystalline anthracene is gratifying. In the case of naphthalene the $^1L_b \leftarrow {}^1A$, $^1B_{3u} \leftarrow {}^1A_g$ transition at 32000 cm.$^{-1}$ [35] (log ϵ 2.4) shows a crystal splitting of 166 cm.$^{-1}$.[4a] A comparison of this weak $^1B_{3u} \leftarrow {}^1A_g$ transition in naphthalene with the very strong $^1B_{3u} \leftarrow {}^1A_g$ transition in anthracene shows that the splitting is approximately proportional to the intensity, if the geometry is similar, in agreement with the Davydov formulation[34] of Frenkel's free exciton theory.[40]

Since the free exciton theory appears to be moderately successful in accounting for the crystal splittings in naphthalene and anthracene, it will now be used to interpret the crystal structure and spectra of acepleiadylene. By analogy with the long-axis transitions in naphthalene and anthracene, the $^1L_b \leftarrow {}^1A$, $^1A_1 \leftarrow {}^1A_1$ "long-axis" transition in acepleiadylene (log ϵ = 3.5) would be expected to show a crystal splitting of approximately 2000 cm.$^{-1}$ if the crystal structure were similar to that of pyrene, provided that the unit cell contained more than one molecule. The polarized absorption spectrum of crystalline acepleiadylene at 77°K. in the cleavage plane is shown in Fig. 6, in which it is compared with the absorption spectrum of acepleiadylene in pyrene. Crystalline acepleiadylene is very strongly dichroic, appearing deep pink-orange for one direction of polarized light and pale yellow-orange for the other. The spectrum of the strongly absorbing component is very similar to the spectrum of the mixed crystal, except that it is shifted slightly (110 cm.$^{-1}$) to lower frequencies. The origin of the strong component of the crystal spectrum is 17670 cm.$^{-1}$. Although the vibrational additions to the electronic transition appear prominently in the strong component and weakly in the weak component, the origin of the strong component does not appear at all in the weak component. In the weak component, the main absorption origin begins at 19560 cm.$^{-1}$ and is much stronger than the bands in the weak component at lower energies. The spectrum in the weak component above 19560 cm.$^{-1}$ resembles the spectrum of acepleiadylene in pyrene shifted to higher energies, and 19560 cm.$^{-1}$ is therefore assigned as the origin of the absorption transition in the weak component. According to this interpretation, the crystal splitting of the 0–0 band is 1890 cm.$^{-1}$, in agreement with expectations. It therefore appears that there is more than one molecule per unit cell in acepleiadylene. The large difference in intensity between the strong and weak components indicates that the symmetry axis of acepleiadylene probably has a much larger projection on one crystal axis in the cleavage plane than on the other, and the large crystal splitting is indicative of a large projection of the molecular symmetry axes of the translationally non-equivalent molecules on each other. In conclusion, the assumption that the crystal structures of acepleiadylene and pyrene are similar appears to be in qualitative agreement with the crystal absorption spectrum.

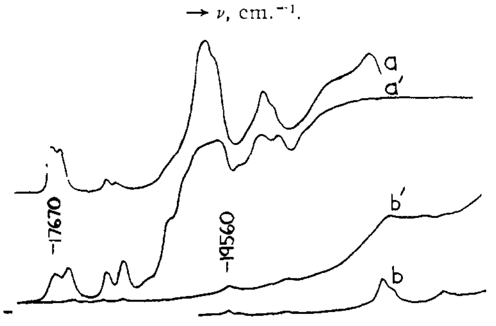

Fig. 6.—The $^1L_b \leftarrow {}^1A$ absorption transition of acepleiadylene in the crystal and in the mixed crystal: (a), (b), *a*- and *b*-axis components, respectively, of mixed crystal with pyrene, 77°K. These spectra have been shifted to coincide with the comparable spectra of the crystal. (a'), (b'), strong and weak components, respectively, of crystal spectra, 77°K.

No fluorescence was observed when crystalline acepleiadylene was illuminated with either blue or ultraviolet light, even though acepleiadylene does fluoresce in the mixed crystal with pyrene or in the rigid glass. Consequently, it is not possible to say anything definite about "trapped excitons"[41] in this crystal.

The crystal spectrum of acepleiadiene shows another effect of the crystal on the molecular transition, *viz.*, crystal-induced mixing of molecular states. This phenomenon has been previously observed in the $^1L_a \leftarrow {}^1A$ transition of anthracene[36] and in the $^1L_b \leftarrow {}^1A$ transition of naphthalene[2] in the crystal state. It is not observed in the spectra of mixed crystals, even though it may be permitted by site symmetry.[15] The polarized absorption spectrum of crystalline acepleiadiene at 77°K. is shown in Fig. 7. The spectrum shows an intensity dichroism, unlike the absorption of the mixed crystal of acepleiadiene in pyrene. The origin in the strong component is 16400 cm.$^{-1}$ which is very

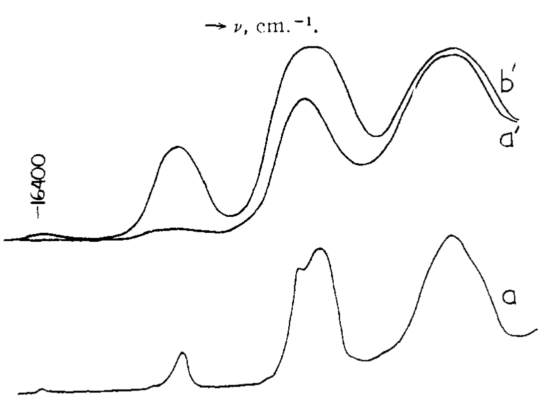

Fig. 7.—The $^1L_b \leftarrow {}^1A$ absorption transition of acepleiadiene in the crystal and in the mixed crystal: (a) mixed crystal with pyrene, 77°K.; (a'), (b'), weak and strong components, respectively, of crystal spectra, 77°K.

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[36] D. P. Craig, *J. Chem. Soc.*, 539 (1955).

[37] L. E. Lyons, *J. Chem. Phys.*, **23**, 1973 (1955).

[38] D. P. Craig, *J. Chem. Soc.*, 2302 (1955).

[39] D. P. Craig and P. C. Hobbins, *ibid.*, 2309 (1955).

[40] J. Frenkel, *Phys. Rev.*, **37**, 17, 1276 (1931).

similar to the origin in the mixed crystal spectrum. The origin appears to be absent from the weak component. Unlike the origin, which is completely polarized, the vibrational structure in the transition becomes increasingly depolarized toward higher energies, indicating a perturbation by a higher transition which is polarized oppositely to the $^1L_b \leftarrow {}^1A$, $^1B_1 \leftarrow {}^1A_1$ transition. The moderately intense transition at 26000 cm.$^{-1}$ (log ϵ 3.5) has been assigned as a $^1L_a \leftarrow {}^1A$, $^1A_1 \leftarrow {}^1A_1$ transition in section (A) of the Discussion. The crystal spectrum for this transition is too broad to enable the origin to be located, but the intensity dichroism is opposite to the $^1L_b \leftarrow {}^1A$ transition in the crystal, in agreement with the $^1L_a \leftarrow {}^1A$ assignment. Therefore, it seems likely that this transition, which is fairly close in energy to and much more intense than the $^1L_b \leftarrow {}^1A$ transition, may be perturbing the higher vibrational levels of the $^1L_b \leftarrow {}^1A$ transition, due to second-order crystal-induced mixing of molecular states belonging to different irreducible representations of the point group of the free molecule.[4a,38] This may occur only if the factor group of acepleiadiene crystal is lower than the assumed C_{2v} symmetry of the free molecule. Further interpretations must await additional knowledge about the structures of these unusual hydrocarbons.

Conclusions

The electronic spectra of acepleiadiene and acepleiadylene have been measured, analyzed and interpreted. The conclusions have been applied to several problems in molecular structure. The results appear to support the Platt FEMO theory and the Moffitt perturbation theory in several respects. It is hoped that additional experimental and theoretical work will lead to a more comprehensive understanding of the properties and structure of pericondensed hydrocarbons.

Acknowledgments.—It is a great pleasure to acknowledge the generosity of Professor V. Boekelheide, who supplied the acepleiadylene and acepleiadiene used in these experiments. The sample of pure pyrene was obtained from Professor M. Szwarc, to whom I am also grateful. Finally, I wish to acknowledge the continued interest and encouragement of Professor A. B. F. Duncan, who greatly facilitated numerous matters connected with the low temperature research.

ROCHESTER, N. Y.

[CONTRIBUTION NO. 454 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Infrared Spectra of Aromatic Compounds. IV. The Nitro Valence Vibrations in *p*-Disubstituted Nitrobenzenes[1]

BY ROBERT D. KROSS AND VELMER A. FASSEL

RECEIVED MARCH 21, 1956

The characteristic nitro asymmetric and symmetric frequencies of *para*-substituted nitrobenzenes are correlated with structure related parameters which are sensitive to the electronic effect of the *para*-substituent on the nitrobenzene nucleus. It is shown that molecular dipole moments, as well as Hammett's σ constants for the *para* groups, yield straight line curves when plotted against the corresponding nitro asymmetric frequency. A plot of nitro asymmetric *vs.* symmetric frequency yields a discontinuous curve, the reasons for which are discussed. Evidence is also presented which places the C–NO_2 stretching frequency in aromatic nitro compounds in the 1300 cm.$^{-1}$ region.

In *para*-substituted nitrobenzenes, the nitro asymmetric stretching vibration usually appears in the frequency range 1500–1560 cm.$^{-1}$. When the *para* substituent is an electron donating group the frequencies fall in the lower end of this range.[2] On the other hand, the nitro symmetric stretching vibration, which usually appears in the 1300–1350 cm.$^{-1}$ region is generally less affected by *para* substituents, although strong electron donors usually give rise to the lowest frequencies. A recent study by Brown[3] related frequency changes in CNO_2 group vibrations to the electronic effects of neighboring constituents. The conclusions reached by Brown agree in principle with interpretations made by us in an independent unpublished study. The data presented in this paper provide a more complete examination of these interpretations as applied to *p*-disubstituted nitrobenzenes and suggest other correlations with structure related parameters. Evidence is also presented which places the C–N stretching frequency in aromatic nitro compounds in the 1300 cm.$^{-1}$ region.

Experimental

Solid spectra of all the compounds as nujol mulls were recorded on a Baird Associates model B double beam infrared spectrophotometer, with a calibration spectrum of polystyrene superimposed on each chart. Chloroform and bromoform, respectively, were used as solvents for obtaining the solution spectra in the 1300–1350 and 1500–1560 cm.$^{-1}$ region. The bands exhibited by chloroform in the 1500–1560 cm.$^{-1}$ region precluded its use as solvent for this frequency range. All solution spectra were obtained with 0.4 mm. cells on a Perkin-Elmer model #13 double beam infrared recording spectrophotometer. The data are presented in Table I.

Results and Discussion

I. The Nitro Asymmetric Stretching Vibration.—Brown[3] has shown that the asymmetric stretching frequency is primarily determined by the N–O bond order, and consequently the N–O stretching force constant. Since bond orders are determined by the relative contribution of reso-

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] (a) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 250. (b) R. R. Randle and D. H. Whiffen, *J. Chem. Soc.*, 4153 (1952).

[3] J. F. Brown, Jr., THIS JOURNAL, **77**, 6341 (1955).