80. V.E.Mironov, F.Ya.Kul'ba, and V.A.Fedorov, Zhur. Neorg.Khim., 9, 1641 (1964) [Russ.J.Inorg.Chem., 888 (1964)].
81. V.E.Mironov, F.Ya.Kul'ba, A.V.Fokina, V.S.Golubeva, and V.A.Nazarov, Zhur.Neorg.Khim., 9, 2133 (1964) [Russ.J.Inorg.Chem., 1152 (1964)].
82. C.W.Gibby and C.B.Monk, Trans.Faraday Soc., 48, 632 (1952).
83. J.C.James and C.B.Monk, Trans.Faraday Soc., 46, 1041 (1950).
84. E.Ya.Ben'yash, Zhur.Neorg.Khim., 9, 2726 (1964) [Russ. J.Inorg.Chem., 1469 (1964)].
85. Z.A.Tyagai, V.S.Galinker, and G.N.Fenerli, Zhur.Neorg. Khim., 7, 1154 (1962) [Russ.J.Inorg.Chem., 593 (1962)].
86. R.L.King, J.Amer.Chem.Soc., 82, 2099 (1960).
87. S.R.Cohen and R.A.Plane, J.Phys.Chem., 61, 1096 (1957).
88. K.B.Yatsimirskii, Symposium, "Termodinamika i Stroenie Rastvorov" (Thermodynamics and Structure of Solutions), Izd.Akad.Nauk SSSR, Moscow, 1959, p.139.
89. R.P.Bell and J.H.B.George, Trans.Faraday Soc., 49, 619 (1953).
90. M.H.Panckhurst and K.G.Woomington, Proc.Roy.Soc., A 244, 124 (1958).
91. C.W.Davies and J.C.James, Proc.Roy.Soc., A 195, 116 (1948).
92. V.P.Vasil'ev and V.N.Vasil'eva, Zhur.Fiz.Khim., 37, 1089 (1963) [Russ.J.Phys.Chem., 571 (1963)].
93. F.Ya.Kul'ba, V.E.Mironov, I.F.Mavrin, Yu.B.Yakovlev, and M.M.Kryzhanovskii, "Tezisy Dokladov Nauchno--Technicheskoi Konferentsii Leningradskogo Technologicheskogo Instituta imeni Lensoveta, 'Khimiya'" (Abstracts of Papers Presented at the Scientific and Technical Conference of the Lensovet Leningrad Technological Institute, "Chemistry"), Moscow–Leningrad, 1964, p.31.
94. F.Basolo and R.G.Pearson, "Mechanisms of Inorganic Reactions", New York, 1958.
95. R.G.Pearson, J.Amer.Chem.Soc., 79, 5382 (1957).
96. C.Postmus and E.L.King, J.Phys.Chem., 59, 1208 (1955).
97. M.Linhard, Z.Elektrochem., 50, 224 (1944).
98. J.C.Bailar and D.H.Busch (Editors), "The Chemistry of the Coordination Compounds" (Translated into Russian), Inostr.Lit., Moscow, 1960.
99. B.Jezowska-Trzebiatowska and M.Wrońska, "XVI Congrès International de Chimie Pure et Appliquée", Paris, 1957, p.827.
100. H.Taube and F.A.Posey, J.Amer.Chem.Soc., 75, 1463 (1953).
101. H.Taube and F.A.Posey, J.Amer.Chem.Soc., 78, 15 (1956).
102. V.E.Mironov, Zhur.Neorg.Khim., 6, 405 (1961) [Russ.J. Inorg.Chem., 205 (1961)].
103. V.E.Mironov, Zhur.Neorg.Khim., 6, 897 (1961) [Russ.J. Inorg.Chem., 458 (1961)].
104. Ya.A.Fialkov and V.B.Spivakovskii, Zhur.Neorg.Khim., 4, 1501 (1959) [Russ.J.Inorg.Chem., 675 (1959)].
105. V.E.Mironov, Zhur.Neorg.Khim., 6, 659 (1961) [Russ.J. Inorg.Chem., 336 (1961)].
106. F.Ya.Kul'ba, V.E.Mironov, and V.N.Pavlov, Zhur. Neorg.Khim., 6, 2814 (1961) [Russ.J.Inorg.Chem., 1420 (1961)].
107. O.Redlich, Chem.Rev., 39, 333 (1946).
108. V.E.Mironov, "Tezisy Dokladov Nauchno-Tekhnicheskoi Konferentsii Leningradskogo Tekhnologicheskogo Instituta imeni Lensoveta, 'Khimiya'" (Abstracts of Papers Presented at the Scientific and Technical Conference of the Lensovet Leningrad Technological Institute, "Chemistry"), Moscow–Leningrad, 1964, p.29.
109. R.A.Plane, "Proceedings of the 8th International Conference on Coordination Chemistry, Vienna", New York, 1964, p.17.
110. V.E.Mironov and V.A.Fedorov, Zhur.Neorg.Khim., 8, 2529 (1963) [Russ.J.Inorg.Chem., 1325 (1963)].
111. V.E.Mironov, Radiokhimiya, 5, 118 (1963).
112. F.Ya.Kul'ba, Yu.B.Yakovlev, and V.E.Mironov, Zhur. Neorg.Khim., 9, 2573 (1964) [Russ.J.Inorg.Chem., 1390 (1964)].
113. V.P.Vasil'ev, Zhur.Neorg.Khim., 7, 555 (1962) [Russ.J. Inorg.Chem., 283 (1962)].
114. T.F.Young, L.E.Moranville, and H.M.Smith, "The Structure of Electrolyte Solutions" (Edited by W.J.Hamer), Wiley, New York, 1959, p.35.
115. L.A.Woodward, "Proceedings of the 8th International Conference on Coordination Chemistry, Vienna", New York, 1964, p.15.
116. J.H.B.George, J.A.Rolfe, and L.A.Woodward, Trans. Faraday Soc., 49, 375 (1953).
117. R.E.Hester, R.A.Plane, and G.E.Walrafur, J.Chem. Phys., 38, 249 (1963).
118. R.E.Hester, R.A.Plane, and G.E.Walrafur, J.Chem. Phys., 40, 411 (1964).
119. S.Fronoeus and R.Larsson, "Proceedings of the 8th International Conference on Coordination Chemistry, Vienna", New York, 1964, p.383.
120. S.Fronoeus and R.Larsson, Acta Chem.Scand., 16, 1433 (1962).
121. R.A.Penneman and E.Staritzky, J.Inorg.Nuclear Chem., 6, 112 (1958).
122. A.B.Lamb and A.T.Larson, J.Amer.Chem.Soc., 42, 229 (1920).
123. "XIX Gertsenovskie Chteniya, 'Khimiya'" [The 19th Gertsen (Herzen) Lectures, "Chemistry"], Gertsen (Herzen) State Pedagogic Institute, Leningrad, 1966, p.10.

Lensovet Leningrad Technological Institute

U.D.C. 543.42.063

ELECTRONIC ABSORPTION AND LUMINESCENCE SPECTRA OF AROMATIC POLYCYCLIC HYDROCARBONS

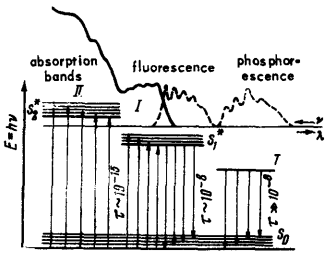
R.N.Nurmukhametov

CONTENTS

1. Electronic states and vibronic spectra of polyatomic molecules 469
2. Benzene and polyacenes 474
3. Angular *ortho*-fused hydrocarbons 476
4. *peri*-Fused hydrocarbons 479

1. ELECTRONIC STATES AND VIBRONIC SPECTRA OF POLYATOMIC MOLECULES

The complete electronic spectrum of a molecule arises from changes in electronic, vibrational, and rotational energy[1-7]. The energy of rotational quanta in polyatomic



molecules is relatively small (the wave numbers corresponding to rotational quanta, which are proportional to their energy, are of the order of $\bar{\nu}_{rot} \simeq 1$ cm^{-1}), and the shape of an electronic band is largely determined by the superposition of the effect of vibrational sub-levels on that of the electronic transition (see Figure). The electronic states of molecules are classified on the basis of the total spin of the electron[1-3,5,6]. As in the case of atoms, a state in which the spins are compensated is called a singlet (S), a state with unit spin is called a triplet (T), and so on. Optical transitions between electronic states in a molecule are controlled by selection rules, according to which transitions between states of the same multiplicity are permitted and transitions between states of different multiplicity are forbidden. Molecular states are further classified on the basis of considerations of the symmetry of the potential field surrounding the nuclear skeleton of the molecule. The symmetry of the wave functions describing particular states of the molecule may not coincide with the symmetry of the skeleton.

In symmetry operations the electronic and the vibrational wave functions undergo similar transformations: hence, classification of these functions and of the states which they describe is possible. We should note that symmetry descriptions are the only precise statements which can be made regarding the wave functions of molecules, since it is impossible, in practice, to obtain the wave functions describing a molecular state in an explicit form. The most convenient classification of states from the point of view of their symmetry is achieved by applying the theory of point groups[1-4,6-8]. Every molecule can be assigned to a definite symmetry group by considering the characteristic symmetry elements of the molecule and symmetry operations. The properties of the transformations of the wave functions stem directly from the concepts of groups. They can be obtained for all groups with which known molecules can be identified. A definite energy state of a molecule with fixed symmetry is called an energy level. The classification of electronic and vibrational states allows us to establish selection rules for optical electronic transitions between energy levels. The probability of a dipolar transition between two states is given by the square of the integral

$$\int \psi^* \hat{\mathbf{M}} \psi^0 \, dv, \qquad (1)$$

where ψ^* is the wave function of the state to which the transition occurs, ψ^0 is the wave function of the initial state, $\hat{\mathbf{M}}$ is the operator of the dipole moment of the transition.

The integral (1) will be non-vanishing if the function within the integral sign (or one of its terms, if the function is in the form of a sum) is fully symmetrical, i.e. if its symmetry properties are identical to those of the molecular skeleton. The function within the integral sign can be fully symmetrical if the product of the terms of the functions under the integral sign ($\psi^* \hat{\mathbf{M}} \psi^0$) gives a fully symmetrical term.

According to the Jahn-Teller theorem[1,2,7], the ground state of a non-linear polyatomic molecule must be non-degenerate and, therefore, fully symmetrical. Hence, a fully symmetrical term will be obtained for the integrand of (1) if the state to which the molecule undergoes a transition from its ground state belongs to the same symmetry type as one of the components of the vector $\mathbf{M}$ (M_x, M_y, M_z in a Cartesian system of coordinates). The selection rules for vibrational-electronic transitions are obtained from formula (1) by putting the wave functions in the form $\psi = \psi_{el}\psi_{vibr}$ (assuming that the rotational state remains unchanged):

$$\int \psi^*_{el} \, \psi^*_{vibr} \, \hat{\mathbf{M}} (\psi^0_{el} \, \psi^0_{vibr}) \, dv. \qquad (2)$$

A purely electronic transition takes place without change in the vibrational state, i.e. $\psi^0_{vibr} = \psi^*_{vibr}$. Multiplication of the vibrational term by itself gives a fully symmetrical term. Therefore, the electronic transition will be allowed if the symmetry of the term ψ^*_{el} coincides with that of one of the components of $\mathbf{M}$ (and the transition will be polarised along the corresponding axis). When an electronic transition is allowed on symmetry grounds, transitions to vibrational sublevels with fully symmetrical terms are also allowed. Vibrations can be active also if they alter the symmetry of the state in such a way that the symmetry of the function $\psi^*_{el}\psi^*_{vibr}$ coincides with the symmetry of one of the other two components of the vector $\mathbf{M}$, the polarisation of the transition changing at the same time by 90°.

If an electronic transition is forbidden on symmetry grounds (so that the purely electronic band is weak, or altogether absent from the spectrum), a vibration of a given symmetry may cause it to become allowed. This requires that the product of the electronic and the vibrational term should belong to the system which describes the transformation of one of the components of $\mathbf{M}$, i.e. should coincide with the symmetry of one of these components. It is evident from formula (2) that strong progressions can occur only with fully symmetrical vibrations, because they do not alter the term in the function within the integral sign even in the overtones. Consider as an example the symmetry group D_{2h}, to which many of the molecules discussed in this review belong. The group D_{2h} includes seven symmetry elements [three mutually perpendicular planes $\sigma(x, y)$, $\sigma(x, z)$, and $\sigma(y, z)$, three second-order symmetry axes c_2^z, c_2^y, c_2^x, and a centre of symmetry], three of which can be independent. Accordingly, eight different types of symmetry are possible, i.e. as many as the number of possible combinations of the signs + and - taken three at a time. Table 1 shows the behaviour of the possible terms of the molecule with respect to symmetry operations.

In the last column of Table 1 the translations T_x, T_y, T_z and the rotations R_x, R_y, R_z are assigned to the symmetry types of pseudo-vibrations. The components of the dipole moment operator $\hat{\mathbf{M}}$ coincide with the components of the vector $\mathbf{T}$. Table 1 shows that the following transitions are allowed for molecules of D_{2h} symmetry: transitions to the state B_{1u} (polarisation along the z axis), to B_{2u} (along the y axis), and to B_{3u} (along the x axis). The products of the various terms can be found from Table 2, which lists the products for the symmetry group.

According to Table 2, in an allowed electronic transition such as A_{1g}-B_{3u} (with polarisation along the x axis)

TABLE 1.

D_{2h}	σ_{xy}	σ_{xz}	σ_{yz}	i	C_2^z	C_2^y	C_2^x	
A_g	+	+	+	+	+	+	+	
A_u	−	−	−	−	+	+	+	
B_{1g}	+	−	−	+	+	−	−	R_z
B_{1u}	−	+	−	−	+	−	−	T_z
B_{2g}	−	+	−	+	−	+	−	R_y
B_{2u}	+	−	+	−	−	+	−	T_y
B_{3g}	−	−	+	+	−	−	+	R_x
B_{3u}	+	+	−	−	−	−	+	T_x

TABLE 2*.

A_{1g}	A_{1u}	B_{1g}	B_{1u}	B_{2g}	B_{2u}	B_{3g}	B_{3u}	
A_{1g}	A_{1u}	B_{1g}	B_{1u}	B_{2g}	B_{2u}	B_{3u}	B_{3g}	A_{1g}
	A_{1g}	B_{1u}	B_{1g}	B_{2u}	B_{2g}	B_{3u}	B_{3g}	A_{1u}
		A_{1g}	A_{1u}	B_{3g}	B_{3u}	B_{3g}	B_{2u}	B_{1g}
			A_{1g}	B_{3u}	B_{3g}	B_{2u}	B_{2g}	B_{1u}
				A_{1g}	A_{1u}	B_{1g}	B_{1u}	B_{2g}
					A_{1g}	B_{1u}	B_{1g}	B_{2u}
						A_{1g}	A_{1u}	B_{3g}
							A_{1g}	B_{3u}

* Taken from Sponer and Teller[7].

we may find, in addition to fully symmetrical vibrations, vibrations of B_{1g} and B_{2g} symmetry, which can alter the polarisation of the band: $B_{3u}B_{1g} = B_{2u}$ (along the y axis) and $B_{3u}B_{2g} = B_{1u}$ (along the z axis).

Sponer and Teller have analysed the electronic–vibrational spectra of many polyatomic molecules on the basis of their symmetry properties, and have tabulated the characteristics and products of various symmetry point groups[7].

Lastly, another important effect of the motion and position of the nuclei on the optical transitions in a molecule is expressed by the Franck–Condon principle: neither the relative position nor the velocity of the nuclei can change appreciably during the transition of a molecule from one electronic state to another, because the transition takes place in a time (10^{-15} s) which is short compared to the vibration period of molecules (10^{-12} s). One consequence of this principle is that molecules can undergo only vertical transitions in the potential energy diagram of the electronic states. Since the molecule spends most of the time at the extreme points (of its vibrations), vertical transitions between points on the potential energy curves are the most probable. If the equilibrium distance r is the same for the ground state and the excited state, bands similar to the purely electronic band will show up most strongly in the spectrum. When r changes appreciably, the purely electronic band becomes weak, even for an allowed transition.

It follows from the Franck–Condon principle, which was formulated in terms of classical physics by simultaneously considering the configurations and velocities of the nuclei, that only fully symmetrical vibrations can be active in electronic–vibrational spectra. Tavger's quantum-mechanical analysis of the Franck–Condon principle[10] has led to the conclusion that active frequencies may include some vibrations which are not fully symmetrical. Obviously the number of active, not fully symmetrical, vibrations must be limited by the selection rules according to the symmetry and structural peculiarities of the molecules.

Absorption and Emission Spectra

Under normal conditions (at room temperature) practically all the molecules remain in the electronic ground state of minimum electron energy. The Boltzmann factor kT is of the order of 200 cm^{-1} for T = 20°C (293°K). Therefore, most of the molecules reside in the zeroth vibrational sublevel of the ground state. For the overwhelming majority of known molecules the ground state is a singlet (S_0). As a consequence of the selection rule, S_i–S_k (i.e. singlet–singlet) transitions have the highest probability. Experiment shows that an excited molecule can remain in the lowest excited S_1^* state for a time $\tau \simeq 10^{-8}$ s, and for even shorter times in higher electronic levels. Hence, no appreciable concentration of molecules in excited states will arise during absorption of light by a system of molecules, and under normal conditions transitions of the type $S_{i>0} \rightarrow S_k^*$ will not occur during absorption, but only transitions from the ground state to excited states: $S_0 \rightarrow S_i^*$. The vibrational structure of an absorption band will be determined mainly by the vibrational sublevels of the excited state (see Figure).

A metastable triplet state may arise in the molecule as a result of non-optical and, to a certain extent, of optical transitions (details of the T-state in the molecule are given below). If a molecule is previously excited to a T-level, it is possible to measure absorption bands for $T \rightarrow T_i^*$ transitions (see Karyakin and Duzhenkov's review[11]). The weak bands of forbidden $S_0 \rightarrow T$ transitions are very much harder to observe.

The frequencies of normal vibrations depend on the electronic state of the molecule. Therefore, the vibrational differences obtained from absorption spectra can be expected to differ from the values for the same vibrations as observed in the vibrational spectra.

The lifetime of a molecule in the excited state and its ability to radiate the excitation energy depend essentially on radiationless deactivation processes. These are strongly dependent on the medium, the temperature, the structure of the molecule, and other factors. Light emission by a molecule is possible if the molecule resides in the excited state for a time $\geqslant 10^{-10}$ s. Experiment shows that a molecule can remain for this length of time only in the lowest S_1^* excited state and in its zeroth (vibrationless) vibrational level. Higher excited S_1^* states and vibrational sublevels undergo radiationless deactivation in shorter time intervals, and light emission from the molecule occurs only from the lowest excited S_1^* state (mainly from a vibrationless level) and from a T-state. Radiation caused by an S_1^*–S_0 transition is termed fluorescence. The structure of the fluorescence spectrum is determined by the active vibrations of the molecules in the ground state; therefore, the frequency values should be close to the frequencies of the same vibrations active in the Raman and infrared absorption spectra. The first, purely electronic fluorescence band, if present, should adjoin the long-wavelength edge of the absorption spectrum (partly overlapping the longest-wavelength absorption band), and the whole of the emission spectrum is located in a longer-wavelength region of the spectrum than the corresponding absorption (Stokes displacement of the emission bands, p. 470). The fluorescence yield is not directly related to the intensity of the long wavelength and other absorption bands. When the radiationless transitions are very weak the excited molecule can remain in a metastable T-state for a longer time (more than 10^{-8} s). The triplet nature

of the metastable state was first pointed out by Terenin[5,12], and subsequently by Lewis[13]. It can be demonstrated experimentally by measuring the magnetic susceptibility of the metastable state of a number of molecules[14,15]; more recently it has been demonstrated by electron spin resonance measurements on molecules of aromatic polycyclic hydrocarbons, and some others[16-18].

Under favourable conditions it is possible to observe an emission band due to a $T \rightarrow S_0$ transition accompanied by radiation and known as phosphorescence. The phosphorescence time can amount to several seconds, since the $T \rightarrow S_0$ transition is forbidden by the selection rule. The transition becomes allowed as a result of spin–orbital interaction. Emission spectra can be observed with opaque, scattering specimens, and, what is even more important, at very low concentrations (in some cases as low as 10^{-12} M). Emission spectra have one limitation: not all molecules can luminesce. An important problem in the field of molecular emission spectroscopy is to identify the conditions which favour the appearance of luminescence. It has been found that with many compounds radiationless deactivation is minimised by working with a solid phase and at low temperatures, thus enhancing the luminescence of the molecules.

Influence of the Medium on the Spectra. Quasi-Linear Structure

In practice one observes the spectra not of a single isolated molecule but of a large assembly of molecules, subjected to various external influences. The spectra of vapours may be thought to be those most closely resembling the spectrum of an individual molecule. However, the spectra of polyatomic molecules are usually diffuse owing to the high temperatures involved (which enhance intramolecular interactions, leading to diffuseness of the bands). Without considering in detail the causes of diffuseness in the spectra of vapours, we shall only point out an obvious cause of "diffuseness" in a vibrational sublevel: the quasi-continuous system of rotational sublevels. This, together with other factors, gives a gaseous system of molecules a spectrum whose structure cannot be properly resolved even with a high-resolution instrument. It should be noted, also, that many compounds are not stable in the vapour state. It is easy to see, therefore, why so few data have been published on well resolved absorption and luminescence spectra of complex molecular vapours, especially of polycyclic aromatic hydrocarbons.

Studies of the spectra of aromatic compounds in a condensed phase are more numerous: liquid and solid solutions, pure and mixed crystals. Under these conditions the spectra are significantly affected by intermolecular interactions, which also cause some diffuseness in the structure of the spectra. The most satisfactory resolution of spectral structure in a condensed phase is obtained at low temperatures for pure or mixed crystals and in neutral, very dilute crystalline solutions. In the latter case we are dealing, figuratively speaking, with a "frozen gas". The spectra of these solutions are either indistinguishable from or slightly shifted towards long wavelengths as compared with vapour spectra. In a condensed phase the molecules are closely spaced, and this hinders or altogether prevents molecular rotations. The earliest studies of quasi-linear electronic–vibrational spectra in crystals are due to Obreimov and Prikhot'ko[19,20]. Spectroscopic studies of pure or mixed single crystals having a crystal lattice of known structure, using polarised light, allow the direction of the moments of electronic transitions to be determined with respect to the axes of the molecule. For aromatic hydrocarbons, investigations of this type have been made by McClure (naphthalene in durene[21], phenanthrene[22]), Sidman (anthracene[23], anthracene in naphthalene and phenanthrene[24], naphthacene in naphthalene[25]), Pesteil and coworkers (see review article[26]), and others.

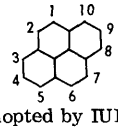
The observation of emission spectra of many aromatic hydrocarbon crystals showing a structure is limited by the photodimerisation effect, involving an excited and a non-excited molecule (excimer formation): the molecular emission band, with a structure, is converted into a structureless emission band at a longer wavelength. This phenomenon has been discussed in detail, for example, in a paper by Stevens[27], but the nature of the phenomenon was made clear by the work of Förster and coworkers[28-31], who studied it in concentrated solutions. Excimer formation from aromatic hydrocarbon molecules in solutions at concentrations above 10^{-3} M suggests the presence of strong interactions involving fluorescing molecules. Therefore, only the spectra of dilute solutions are similar to the spectra of undisturbed molecules. Polarisation measurements on the spectra, enabling the relative polarisation of the various electronic transitions to be determined, are also possible in the case of solutions.

In a series of investigations[32-38], Zimmerman and Yoop have examined the polarisation of the absorption and fluorescence spectra of alcoholic solutions of benzene, naphthalene, anthracene, naphthacene, phenanthrene, 1,2-benzanthracene, chrysene, pyrene, perylene, triphenylene, coronene, and azulene at -180°C. In every case they were able to show that the singlet–singlet bands are polarised in the plane of the molecule. Dörr and coworkers[39-41] showed that the moment of the T–S_0 transition for a series of aromatic hydrocarbons is polarised along a direction normal to the plane of the molecule.

There is no general method for obtaining spectra with an optimum degree of resolution of the vibrational structure, and the problem has to be approached empirically for each individual compound. Shpol'skii and coworkers made an important contribution in this field when they obtained, in 1952, quasi-linear fluorescence spectra for coronene and 3,4-benzopyrene† [42] in crystalline solutions at 77°K. They observed a splitting of the bands into multiplets which has since become known as the Shpol'skii effect. We shall not dwell on the specific features and on the nature of band multiplicity: interested readers are referred to existing review articles[43].

The n-hydrocarbon class of inert solvents has been very useful for resolving the structure of the spectra of many compounds: the study of spectral structure in n-hydrocarbons at low temperatures (77°, 20°, and 4°K) is called the Shpol'skii method. Shpol'skii and his school studied the quasi-linear spectra of many aromatic hydrocarbons[44-66]; their results are used in the present review. In a series of papers[67-69] Sponer, Kanda, and their coworkers showed

† The numbering of the pyrene ring system used by the author is evidently



which is contrary to that adopted by IUPAC and the Chemical Society (Ed. of Translation).

TABLE 3. Frequencies (cm^{-1}) of the electronic $S_1^*-S_0$ and $T-S_0$ transitions of aromatic hydrocarbons.

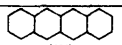
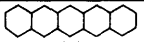
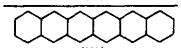
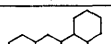
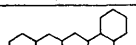
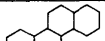
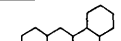
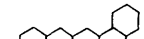
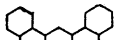
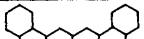
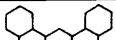
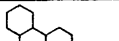
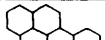
Formula	$\nu_{S_1^*-S_0}$ and medium	References	ν_{T-S_0} and medium	References	$\nu_{S_1^*-T}$	
 (I)	37800 fl. and abs., hex.	90	29500 cycl.	67	8300	
 (II)	31730 fl. and abs., pent.	51	21300 PE	102	10430	
 (III)	26240 fl., hept.	52	14930 EPA	107	11310	5490/6370
 (IV)	21160 fl., non.	51	10500	80	10660	5080/4430
 (V)			8000	80		
 (VI)	14430 abs.					
 (VII)	28820 fl., pent.	71	21770 hex. 21800 pent. 21640	71 78	7020	
 (VIII)	26000 abs. and fl., alc.	35	16520 16700	78	9300	
 (IX)						
 (X)	27800 fl., oct. 27900 fl., alc.	64 35	20000 oct. 19800 alc. 20040	64 40 78	7800 8100	
 (XI)	25300 25440 abs. and fl., pent.	53	18300 18260		7000	
 (XII)	22850 abs. 23000 fl.	73 117				
 (XIII)	26870	73	20020 20200	78 119	6670	
 (XIV)	25310 25350	73 117	18500 17900	78	7450	
 (XV)	23120	73				
 (XVI)			20550 alc.	174		
 (XVII)			20080	44 45		
 (XVIII)	26840 fl. and abs., hex. 26850 fl.	55 36	16900 hex. 16850		9940	
 (XIX)	26570 fl., hex.	46	18630 hex. 18510	46	7940	
 (XX)	24850 fl., hept.	47	14670	119	10180	

TABLE 3 (contd.)

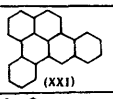
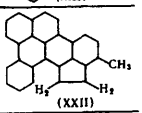
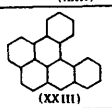
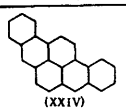
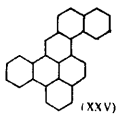
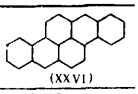
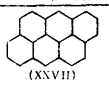
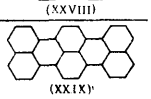
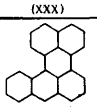
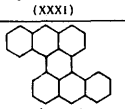
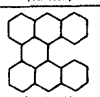
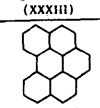
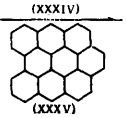
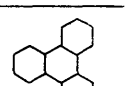
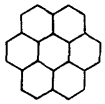
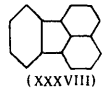
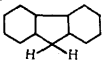
Formula	$\nu_{S_1^*-S_0}$ and medium	References	ν_{T-S_0} and medium	References	$\nu_{S_1^*-T}$
 (XXI)	25250 fl., oct.	56	17000		8250
 (XXII)	25065 fl., oct.	59 60	16450	59 60	8615
 (XXIII)			14570	119	
 (XXIV)			14050	119	9000
 (XXV)	23920 fl. and abs., hex.	60	16915	60	7005
 (XXVI)	22460 fl., hex.	49 56	12040	119	10420
 (XXVII)	23250		11850	119	11400
 (XXVIII)	22450 fl. and abs., hex. 22700 fl. and abs., alc.	62 36	12600	80	10000
 (XXIX)	18960 abs.				
 (XXX)	15090 abs.				
 (XXXI)	19450 abs.				
 (XXXII)	17920 abs.				
 (XXXIII)	18310 abs.				
 (XXXIV)	24625 fl. and abs., hex.	58	16250 hex. 16180	58	8375
 (XXXV)	15740 abs.				
 (XXXVI)	29100 fl. 29140 fl., hex.	120	23800 23590 hex. 23250	120 174	5300 5550

TABLE 3 (contd.)

Formula	$\nu_{S_1^*-S_0}$ and medium	References	ν_{T-S_0} and medium	References	$\nu_{S_1^*-T}$
 (XXXVII)	23 500 fl., hex.	44	19 375 hex. 19 040	50	4125
 (XXXVIII)					
 (XXXIX)	33 160 fl. and abs., hex.	61	23 790 hex.	61	9370

The abbreviations specify the spectra from which the electronic transition frequencies were determined and the solvent used: abs. — absorption spectrum; fl. — fluorescence spectrum; hex. — hexane; PE — petroleum ether; EPA — ether–isopentane–alcohol; oct. — octane; hept. — heptane; pent. — pentane; non. — nonane; cycl. — cyclohexane; alc. — alcohol.

that frozen cyclohexane is a good matrix for resolving the structure of the phosphorescence spectra of various compounds. The present writer has shown, for the case of pyrene in polyisobutylene[62,63], that quasi-linear structure can be obtained also in a polymeric matrix. Bowen and Brocklehurst[70], and also Pesteil and Rabaud[71], have used Shpol'skii's method to obtain quasi-linear spectra for a series of aromatic hydrocarbons.

Among organic compounds which absorb in the visible and near ultraviolet region of the spectrum, aromatic hydrocarbons are the simplest in the sense that their electronic bands in that region are associated with a single type of transition ($\pi-\pi^*$). The problem of establishing the relationship between structure and spectra amounts to formulating the influence of conjugation type (including the geometry of the conjugated system of π-electrons) upon the electronic bands. Polycyclic, fused hydrocarbons have a rigid planar structure which favours the appearance of a vibrational band substructure. The vibrational structure of bands of this class of compounds arises primarily from fully symmetrical vibrations of the carbon skeleton of the molecule (ν_{C-C}). In these cases we can apply a classification in terms of the symmetry of the energy states and establish selection rules for the particular molecule. Practically all known hydrocarbons exhibit fluorescence, and many also phosphorescence (under certain conditions). There is published information both on the absorption and on the luminescence spectra of this class of compounds. Inspection of the relation between the spectra and the structure of the molecules has shown a tendency for the absorption and fluorescence bands in aromatic hydrocarbons to be shifted towards longer wavelengths as the number of benzene rings and of conjugated double bonds in the skeleton of the molecule increases. When the arrangement of benzene nuclei is non-linear the wavelength displacement rule for the electronic bands becomes more complicated. Clar has described the absorption spectra and classified the absorption bands of aromatic hydrocarbons empirically on the basis of intensity differences, differences in the degree of the bathochromic shift with increase in the size of the π-electron system of the molecule, and differences in band shift on going from vapours to solutions[72-77].

α-Bands have a small extinction coefficient ($\log\epsilon \simeq 2.3-3.3$) and appear at the longest wavelengths for many hydrocarbons. On increasing the length of the linear chain of benzene rings, the α-band is usually obscured by a stronger p-band. p-Bands of average intensity ($\log\epsilon \simeq 3.6-4.1$) move rapidly towards longer wavelengths on increasing the linear condensation of nuclei. β-Bands of high intensity ($\log\epsilon \simeq 4.5-5.2$) undergo shifts similar to those of the α-bands as the number of benzene nuclei is increased.

Clar and Zander[78] have collected and discussed the data on phosphorescence spectra for a series of polycyclic hydrocarbons. They point out that the frequency differences between p-bands and the triplet level (of the order of $10-12\times10^3$ cm^{-1}) are approximately constant; T-level positions are listed in other papers[79,80].

Many theoretical discussions of the electronic states and spectra of aromatic hydrocarbons are available: these rely on concepts of the covalent bond, molecular orbitals, and the free electron model. Platt has proposed a perimetric model of the free electron for *ortho*-fused hydrocarbons; with this model, he has calculated the polarisation energies and classified the electronic transitions of many hydrocarbons[81,82]. Platt's band designations ^1L_b, ^1L_a, ^1B_b, ^1B_a, where the subscripts a and b denote polarisation along a particular axis of the molecule, are adopted in the present article. Platt[83] calculated the molecular orbitals by the simple one-electron LCAO method, and also considered[84] the transitions in *peri*-fused hydrocarbons. Ham and Ruedenberg[85] calculated the electronic states of aromatic hydrocarbons on the basis of antisymmetric products of free-electron molecular orbitals. This led to a slight modification of Platt's band classification: their values are shown in brackets in the present article.

There are also theoretical calculations by Pariser[86] and Moffit[87]. An unusual evaluation of transition energies in aromatic hydrocarbons, based on calculated resonance energies of structures in an excited state, has recently been carried out[88].

Table 3 lists the data on the energy of $S_1^*-S_0$ and $T-S_0$ transitions for a number of hydrocarbons.

2. BENZENE AND POLYACENES

From the point of view of electronic spectra, the polyacene series should be regarded as beginning with naphthalene rather than benzene, because all polyacene molecules (except benzene) belong to the same symmetry group D_{2h}.

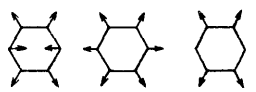
The benzene molecule (I)‡ has the D_{6h} symmetry.

In absorption, benzene shows three bands in the region of 2600, 2000, and 1800 Å. The band at 1800 Å ($\log\epsilon \simeq 4.6$) is ascribed to the $A_{1g}-E_{1u}$ transition. The transition is allowed by symmetry and is polarised in the plane of the molecule[89]. The second band at 2000 Å ($\log\epsilon \simeq 3.6$) is resolved into diffuse bands and is associated with the $A_{1g}-B_{1g}$ transition, forbidden by symmetry. The symmetry properties of the B_{1g} state correspond to an alternating distribution of electron density. The symmetry bar

‡ Here and elsewhere in this article, molecules are numbered as in Table 3.

is removed by a vibration of the e_g^+ type. Vibrational series of 160 and 965 cm^{-1} have been identified[89,90]. The weak long-wavelength band of benzene at 2600 Å has been the object of many investigations (see, for example, the review by Jones and Spinner[106]), and has been assigned to the $A_{1g}-B_{2u}$ transition, forbidden by symmetry. In the vapour phase this band is found to split into many narrow bands. A detailed vibrational analysis of this band has been made[7,91], and the vibrations have been assigned to symmetry types It has been shown that the symmetry bar is removed by a vibration of the e_g^+ type, having a frequency of 520 cm^{-1} in the S_1^* state. The fundamental series in the spectrum is determined by fully symmetrical vibrations of frequency 923 cm^{-1}, and begins at the frequency $\nu = \nu_{00} + \nu_{e_g^+} = 38\,089 + 520$ cm^{-1} (for the vapour).

The 923 cm^{-1} vibration corresponds to a "breathing" vibration of the ring



520 + 923 = 1443 (in the S_1^* state); 606 + 992 = 1600 cm^{-1} (in the S_0 state).

The frequency 1600 cm^{-1} is often very active in the spectra of compounds containing benzene rings. The weak fluorescence band of benzene, in the region of 2700–3100 Å, is associated with the same $B_{2u}-A_{1g}$ transition, forbidden by symmetry. In emission the transition becomes allowed as a result of the e_g^+ vibration of frequency 606 cm^{-1}, but the fundamental series is associated with a vibration at 992 cm^{-1}. The structure of the fluorescence spectrum of benzene is well resolved at 77°K in cyclohexane solution. According to Braude[90], in hexane the ν_{00} frequency of the $S_1^*-S_0$ transition is 37 800 cm^{-1}. A phosphorescence spectrum with a structure has been obtained[92] in a matrix of cyclohexane at 77°K (and also[67] at 77° and 4.2°K). The $T-S_0$ spectrum has been interpreted by Sponer and coworkers[67] starting with the doublet at 29 501/29 442 cm^{-1}, referred to the 00 band, with the help of the e_g^+ vibration frequencies 607, 1178, 1590/1607 cm^{-1}, of the b_{2g} vibration frequencies 698, 988, 1458 cm^{-1}, and of the series of fully symmetrical vibrations (frequency 992 cm^{-1}). A vibrational analysis of $T-S_0$ spectra has also been given by Shull[93] and by Dikun and Sveshnikov[94].

The frequency difference $\nu_{S_1^*-T}$ in benzene amounts to 8300 cm^{-1}.

Naphthalene (II). Symmetry D_{2h}. Three electronic bands can be distinguished in the absorption spectrum[73]: ^1L_b (31 750), ^1L_a (34 500), ^1B_b. The most intense short-wavelength band at 220 nm is practically structureless, and is associated with the $A_{1g}-B_{3u}$ transition, polarised along the long axis of the molecule[21,32]. The broad ^1L_a band in the region of 2900–2300 A, with a weakly developed vibrational structure, is associated with the $A_{1g}-B_{3u}$ transition, polarised along the x axis, as shown by McClure[21] in his study of the absorption spectrum in polarised light of a mixed naphthalene–durene single crystal, and by Zimmerman and Yoop[32] on the basis of polarisation absorption and luminescence spectra of solutions at -180°C. The weakest long-wavelength absorption band (3300–2900 Å) has a sharp vibrational structure in many solutions at low temperatures, and is ascribed to an $A_{1g}-B_{2u}$ transition. McClure[21] separated two series of bands in the vibrational structure: a series of weak bands, beginning from the purely electronic band, polarised along the y axis, and a stronger series of bands, whose origin lies 509 units higher (on the cm^{-1} scale) than the 00 band. The 3300 Å fluorescence band of naphthalene, associated with the same $B_{2u}-A_{1g}$ electronic transition as the long-wavelength absorption, also has a well developed vibrational structure. Bolotnikova[51] has described the quasi-linear structure of the fluorescence band in pentane solution at 77°K. McClure distinguished two systems, having mutually perpendicular polarisations, in the fluorescence spectrum. Similar results were obtained by Bolotnikova in her vibrational analysis of fluorescence in pentane. She identified the most active frequencies (517, 772, 1033, 1386, 1465, and 1579 cm^{-1}) and assigned them to fully symmetrical skeletal vibrations. The 500 cm^{-1} interval by which the origin of the second series is separated from the 00 band (ν_{00} = 31 731 cm^{-1}) was assigned to a vibration of b_{1g} symmetry. Papers on the long-wavelength absorption[95] and emission[96-98] bands of naphthalene vapour give a detailed vibrational analysis of the electronic bands. The results for vapour spectra agree with the analysis of solution spectra: two series of bands, with a 506 cm^{-1} difference in relative position, can be distinguished also in the spectra of the vapour. (In the vapour, ν_{00} for the long-wavelength transition is 32 017 cm^{-1}). The vibration frequencies obtained from an analysis of the vibronic spectra are in good agreement with the frequencies obtained from the vibrational spectra of naphthalene[99] and also with the theoretically calculated values[100,101].

The phosphorescence spectrum in a propyl ether–isopentane solution at -190°C begins with a strong band ($\nu_{00} \simeq$ $\simeq$ 21 300 cm^{-1}) and can be resolved into 20 bands, interpreted[102,103] in terms of the frequencies 512, 1146, 1380, and 1575 cm^{-1}.

Anthracene (III). The absorption spectrum is characterised by three electronic bands with a sharply resolved vibrational structure: ^1L_a (26 000), ^1B_b (40 400), $^1C_b(^1B_a)$ (45 000 cm^{-1}).[73]

Sidman[24] measured the absorption bands in polarised light for anthracene–naphthalene and anthracene–phenanthrene crystals, and showed that the transitions ^1L_a and $^1C_b(^1B_a)$ are polarised along the x axis, whereas the ^1B_b transitions are polarised along the y axis. These results were confirmed[32] by measurements of the absorption and fluorescence polarisation spectra of solutions, and also[104] by measuring the dichroism of the absorption bands in stretched films. Polarisation of a similar type was observed also for pure single crystals of anthracene[23,105]. Jones and Spinner[106] give an analysis of the structure of the absorption bands in pentane solution at -100°.

p-band: $\nu(26\,570 + 390n_1 + 790n_2 + 1440n_3)$ cm^{-1} ($n_1 = n_2 = 0,1$; $n_3 = 0-5$).

β-band: $\nu(39\,460 + 300n_1 + 1070n_2 + 1370n_3)$ cm^{-1} ($n_1 = n_3 = 0,1$).

A detailed analysis of the long-wavelength band, associated with the $A_{1g}-B_{3u}$ transition, was published by Sidman[24] for a mixed crystal at 4°K and by Bolotnikova[52] for a heptane solution at 77°K. The structure is determined mainly by a 1400 cm^{-1} series, assigned to a fully symmetrical vibration.

The blue fluorescence band of anthracene lies almost entirely in the visible region of the spectrum. The best resolution of this structure was obtained[52] in solution at

77°K, when the purely electronic band (26241 cm^{-1}) was separated from the vibrational frequencies (390, 1037, 1165, 1407, 1565, 1645 cm^{-1}), assigned to fully symmetrical vibrations. Sidman[24] gave an analysis of the fluorescence band of anthracene in a mixed crystal. It is interesting to note that the 403 and 1416 cm^{-1} frequencies in the spectrum of the mixed crystal are reduced to 390 and 1407 cm^{-1} in the spectrum of the heptane solution. Intense series in the fluorescence band are associated with the frequency 1407 cm^{-1}.

Zimmerman and Yoop[32] analysed the structure of the band in absorption and in emission on the basis of polarisation spectra of the solution at -180°C. They resolved two series of bands, polarised in mutually perpendicular directions. The main series, with its origin in the 00 band, is polarised along the x axis: $\nu_N = \nu_{00} \pm n_1\nu_1 \pm n_2\nu_2$ (ν_{00} = = 26000 cm^{-1}, ν_1 = 1400, n_1 = 0, 1, 2; ν_2 = 500, n_2 = 0, 1), and the subsidiary series has $\nu_N = \nu_{00} \pm 900 \pm n_1\nu_1 \pm n_2\nu_2$, polarised along the y axis (the + sign refers to the absorption bands, the - sign to the emission bands). As in the case of naphthalene, the difference of 900 cm^{-1} must be assigned to a vibrational frequency of b_{1g} symmetry. The same authors[32] point out certain minima in the polarisation absorption spectra at 28500 and 30000 cm^{-1}, which they tentatively ascribe to a ^1L_b transition in absorption, since according to theory the weak ^1L_b band should be hidden by the ^1L_a band.

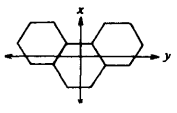
Anthracene has a phosphorescence band in the infrared region. The structure of the T–S_0 spectrum has been described[107] in terms of an initial band at 14928 cm^{-1} and vibrational frequencies of 410, 1137, 1266, 1414, and 1573 cm^{-1}. The transition is interpreted as $^3B_{2u}$–$^1A_{1g}$, and the frequencies are assigned to fully symmetrical vibrations.

Naphthacene (IV). ^1L_b and ^1L_a bands have been identified[73] in the absorption spectrum. According to theory, the weak $^1L_b(\alpha)$ band is concealed by the ^1L_a band. Studies of the polarisation of the spectra of naphthacene in naphthalene have shown[25] that the ^1L_a band is polarised along the short x axis, whereas the ^1L_b and ^1B_b bands are polarised along the y axis. Sidman gives a detailed analysis of the structure of the long-wavelength absorption and fluorescence bands of a mixed crystal. Bolotnikova[52] analysed the vibrational structure of the given fluorescence spectrum of naphthacene in nonane at 77°K, and found a structure identical to that of the fluorescence in naphthalene. She isolated the frequencies at 321, 462, 615, 1165, 1473, and 1380 cm^{-1}. The intense series of the last frequency determines the form of the fluorescence spectrum. The data on the polarisation of the electronic transitions were confirmed by Zimmerman and Yoop[32]. The weak minima at 25000 and 26400 cm^{-1} in the polarisation absorption spectra are ascribed to a ^1L_b transition. The same authors also describe[32] the vibrational structure of the polarisation fluorescence spectrum. The initial band at 20000 cm^{-1} consists of two superimposed bands with mutually perpendicular polarisation, from which two series of bands with a 1400 cm^{-1} period originate. Only a calculated value (~10500 cm^{-1}) of the energy of the T–S_0 transition appears to be known[80]. The quoted value[79] ν_{phos} = 19600 must be ascribed to impurity phosphorescence. Clar and Zander[78] have shown that the phosphorescence bands disappear upon careful purification of naphthacene. It has been suggested[60] that the impurity is naphthacenequinone.

The long-wavelength band of pentacene (V) extends over the whole of the visible region 6000–4000 Å (the T-level[80] is in the region of 8000 cm^{-1}). The last of the polyacenes which have been prepared, hexacene (VI), absorbs[73] in the region 7000–5500 Å ($\nu_{S_1^*-S_0} \simeq 14430$ cm^{-1}). Polyacenes with a larger number of rings are unstable. The long-wavelength absorption band and the fluorescence spectrum of anthracene, naphthacene, and pentacene show a similarity in their vibrational structure, which is determined mainly by a vibrational difference of 1400 cm^{-1}. In the polyacene series (benzene, naphthalene, anthracene, naphthacene, pentacene, and hexacene) the energy of the S_1^*–S_0 and T–S_0 transitions decreases as the number of benzene rings increases by the following amounts respectively: 6300 (8000 for T–S_0), 7000 (6600), 5000 (4000), 4000 (2500), 3000 cm^{-1} (see Table 3). The drop in energy becomes gradually smaller as the number of rings increases. At the same time, the energy difference between the S_1^* and the T states retains its value (10000 cm^{-1}) practically unchanged, with only a slight decrease.

3. ANGULAR *ortho*-FUSED HYDROCARBONS

Phenanthrene, of C_{2v} symmetry, the simplest angular hydrocarbon, is an isomer of anthracene. It was originally suggested that its spectroscopic characteristics should be similar to those of anthracene. In practice, its spectra are much more complicated, and quite different from those of anthracene. The bands of four electronic transitions can be distinguished in the absorption spectrum: ^1L_b, ^1L_a, ^1B_b, and $^1C_b(^1B_b)$. Calculation predicts that the ^1L_b and $^1C_b(^1B_b)$ transitions should be polarised along the x axis, whilst the ^1L_a and $^1B_b(^1B_a)$ transitions are polarised along the y axis. McClure studied the spectrum of the ^1L_b absorption band of a crystal at 20°K in polarised light, and showed[22] that the band of the 00 transition (28660 cm^{-1}) is polarised along the x axis. It follows from measurements of the polarisation absorption spectra in ethanol solution at -180°C that the 00 band of the ^1L_b transition is polarised at right angles to the bands of the ^1L_a (3400 cm^{-1}) and ^1B_b (39300 cm^{-1}) 00 transitions. Zimmerman and Yoop[35] report that weak bands at 34900 and 38200 cm^{-1}, polarised along the x axis, are also present in the spectrum. The ^1L_b band has a clearly defined vibrational structure in the polarisation spectrum, due to the presence of two series of bands polarised in mutually perpendicular directions. The main series begins at the 00 band: ν_N = 28900 cm^{-1} + + $n_1\nu_1$(ν_1 = 1400 cm^{-1}; n_1 = 0, 1, 2). The origin of the secondary series differs by 700 cm^{-1}: ν_N = 28900 + 700 + + $n_1\nu_1$. Popov[104] studied the dichroism of absorption bands in stretched films and showed that the ^1L_b transition is polarised along the x axis, whilst the ^1L_a and ^1B_b transitions are polarised along the y axis. He also discovered in the dichroism curve a structure within the ^1L_b band, which he associated with the appearance of a not fully symmetrical vibration at 670 cm^{-1}.



Later workers obtained a better resolution of the vibrational structure of this band, and showed that it arises from the large number of frequencies which are active in the vibrational spectrum. McClure published an analysis

of the structure of the absorption band of crystalline phenanthrene[22]. Kharitonova[108] examined the structure of the absorption bands of the vapour, and distinguished the frequencies ν_{00} = 29 120 cm^{-1} and ν_{vibr} = 680 and 1420 cm^{-1} in the ^1L band. In the second band, with $\nu_{00} \simeq$ 35 200 cm^{-1}, she found ν_{vibr} = 360, 470, 680, 960, and 1400 cm^{-1}.

The fluorescence spectrum, investigated under a variety of conditions, shows a well resolved vibrational structure. The polarisation structure of the fluorescence spectrum[35] indicates the presence of two series of bands, polarised at right angles to each other. The main series begins at the 00 band, and the origin of the second series is separated from it by the frequency of a vibration of b_2 symmetry whose value could not be accurately determined.

Pesteil and Rabaud[71] obtained an extensive quasi-linear structure in the fluorescence band of a pentane solution at 20°K. The spectrum, with a band head at 28 818 cm^{-1}, was interpreted with the help of more than 30 frequencies, some of a_1 symmetry, and some apparently b_2 symmetry. The authors[71] also made a detailed analysis of the phosphorescence spectrum under the same conditions, found in a region of lower frequencies (~7020 cm^{-1}). Kanda and Shimada[109] analysed the T–S_0 spectrum in ether–isopentane–alcohol and in petroleum ether media at 90°K. In solution in polypropyl ether–isopentane the phosphorescence band splits into 16 bands at 77°K: $\nu_{00} \simeq$ 21 730, $\nu_{vibr} \simeq$ 406, 1417, 1608 cm^{-1}. According to Cropper and Dörr[39], the T–S_0 transition is polarised at right angles to the plane of the molecule, and some not fully symmetrical vibrations are active in the T–S_0 spectrum in addition to the fully symmetrical vibrations. As regards phosphorescence, phenanthrene shows some further differences from anthracene. The initial band of its bluish-green phosphorescence lies at even higher frequencies than the green phosphorescence band of naphthalene. These facts suggest that Clar's hypothesis[74], according to which the π-electron cloud of phenanthrene can be regarded as the π-electron cloud of biphenyl plus an ethylene group (for the ground state of the molecule), is not applicable to these spectra. The long-wavelength transitions of biphenyl and phenanthracene are polarised at right angles to each other, but the energy of the transition is higher in biphenyl than in naphthalene, whilst it is lower in phenanthrene. We should note that the spectroscopic characteristics of phenanthrene are, perhaps, closer to those of naphthalene than to those of anthracene. This similarity between the spectra of 1,2-benzopolyacenes and those of the parent polyacenes becomes even more apparent with longer polyacene units.

1,2-Benzanthracene (tetraphene) (VIII). Four absorption systems have been distinguished in the absorption spectrum: ^1L_b, ^1L_a, ^1B_b, and $^1C_b(^1B_a)$. The 00 bands for these transitions in alcohol solution at -180°C occur[47] at 26 000 cm^{-1} for ^1L_b, 27 300 cm^{-1} for ^1L_a, 34 400 cm^{-1} for ^1B_b, and 43 500 cm^{-1} for ^1C_b. Experimental data on the polarisation of the electronic bands are in approximate agreement with theory[100], but they give somewhat different values for the angles between the polarisation vectors[35]. The regions of the different mutually overlapping electronic bands have been identified[110] from the temperature dependence of the spectra. The results[100], given in Table 4, do not agree entirely with the analysis of the bands[35].

Sandorfy and Jones[111] have analysed the absorption spectra in pentane at -100°C in the region 26 000–33 000 cm^{-1}, and have distinguished two series of bands with a spacing of 1400 cm^{-1}.

TABLE 4.

Band region (cm^{-1})	Type (after Zhirnov[100])	Type (after Craig et al.[98])
26 000–31 000	^1L_b	α
27 000–33 000	^1L_a	p
33 000–35 000 (Possibly 37000)	^1B_b	
33 000–38 000	^1B_a	β
	Three other electronic band systems were not interpreted	

The fluorescence spectrum[111,112] of a solution at room temperature consists of wide bands with ν_{00} = 26 000 cm^{-1} and an interband spacing ν_{vibr} = 1400 cm^{-1}. The first phosphorescence band has a frequency about 9500 cm^{-1} lower than the fluorescence band[102,113]. In solution in isopentane–methylcyclohexane (1 : 4) at 77°K the phosphorescence spectrum shows three maxima: at 6060 (15 500 cm^{-1}, 6570, and 7250 Å. In a propyl ether–isopentane solution the phosphorescence band splits into 6 bands in the region of 16 700 (ν_{00})–11 200 cm^{-1}; their frequencies are given by the series $\nu = (\nu_{00} - 400n_1 - 1350n_2)$ cm^{-1}.

The T level in 1,2-benzanthracene is found to be somewhat higher than in anthracene (just as it is higher in phenanthrene than in naphthalene). Angular fusion of a benzene ring in the 1,2-position in polyacenes is accompanied by an increase in the relative height of the T level, or by a decrease in the difference $\nu_{S_1^*-T}$. For the longer polyacenes [1,2-benzonaphthacene (IX), 1,2-benzopentacene], only the absorption spectra are known. The long-wavelength bands are fairly similar in position and vibrational structure to those of the parent polyacenes. We shall now consider angular molecules formed by a centro-symmetrical combination of benzene rings.

Chrysene (X). Symmetry C_{2h}. The absorption spectrum contains four electronic bands: ^1L_b, ^1L_a, ^1B_b, $^1C_b(^1E_a)$.

An analysis of the polarisation absorption and fluorescence spectra gave approximate agreement with theory, with slightly different values of the angles[35]. The following values are reported[35] for the 00 band frequencies: 27 800 cm^{-1} for ^1L_b, 30 900 cm^{-1} for ^1L_a, 37 000 cm^{-1} for ^1B_b, and 44 100 cm^{-1} for $^1C_b(^1B_a)$. Although the chrysene molecule contains four benzene rings, the long-wavelength transition in this molecule has an energy intermediate between those of phenanthrene and anthracene. The vibrational structure of the ^1L_b absorption band has been analysed[64] as for the crystalline state.

The structured band spectrum of the deep blue fluorescence[13,114] in solution in ether-isopentane–alcohol at -190°C begins with a band having $\nu_{00} \simeq$ 27 800 cm^{-1}. The difference ν_{vibr} = 1370 cm^{-1} has been identified[115] in the fluorescence spectrum of the crystals. Nurmukhametov and coworkers[64] have analysed the vibrational structure of the quasi-linear fluorescence spectrum in octane solution at 77°K, and have identified the vibrational frequecies 295, 875, 1180, and 1395 cm^{-1}, the last being the most characteristic of the spectrum. Two series of bands, polarised at right angles to each other, have been detected[35] in the polarisation fluorescence spectra of an alcohol solution at 90°K: $\nu_N = \nu_{00} - n_1\nu_1$ (ν_{00} = 27 900, ν_1 = 1400) cm^{-1}, n_1 = = 0, 1–3; $\nu_N = \nu_{00} = 800 - n_1\nu_1$. Dörr and Cropper[40]

have demonstrated the presence of two subsidiary series with identical polarisation: $\nu_{N'} = \nu_{00} - 300 - n_1\nu_1$ and $\nu_{N''} = \nu_{00} - 800 - n_1\nu_1$ (where $\nu_{00} = 27\,800$, $\nu_1 = 1400$ cm^{-1}, $n_1 = 0,1-4$).

The T level in chrysene is lower than the S_1^* level by 7500 cm^{-1}, i.e. approximately by the same amount as in phenanthrene. The vibrational structure of the phosphorescence band in octane solution has been analysed[35] in terms of the frequencies $\nu_{vibr} = 300$, 646, 1230, 1375, and 1617 cm^{-1} ($\nu_{00} = 20\,000$ cm^{-1}). The phosphorescence in ether–isopentane–alcohol at -190°C has been described. Measurements of the polarisation phosphorescence spectra[40] have shown that the $T-S_0$ transition is polarised at right angles to the plane of the molecule, and in alcohol solution has the frequency $\nu_{00} \simeq 19\,800$ cm^{-1}. The phosphorescence spectrum shows a definite similarity to the phosphorescence spectrum of phenanthrene. The frequencies 300 and 375 must be assigned to not fully symmetrical vibrations, the remainder to fully symmetrical vibrations.

1,2;5,6-Dibenzanthracene (XI). Symmetry C_{2h}. Clar distinguished three electronic bands in the absorption spectrum of its benzene solution: α (with maxima at 3950, 3850, 3730 Å), p (3510, 3365, 3220 Å), and β (3000, 2900, 2770 Å).

Bolotnikova[53] analysed the vibrational structure of the long-wavelength absorption band in pentane at 77°K, assigned the 25 441 cm^{-1} band to a 00 transition, and identified the differences 488, 605, 691, 748, 1355, 1445, and 1586 cm^{-1}. The fluorescence band of the solution at room temperature consists of three maxima[117] (25 400, 24 000, and 22 500 cm^{-1}); at 77°K the band splits, in hydrocarbon or alcoholic solutions, into 13 bands[118], and in pentane–octance solutions it splits into a large number of bands with initial $\nu_{00} \simeq 25\,442$ cm^{-1}. In the vibrational structure the following differences have been identified: 220, 320, 453, 495, 544, 588, 620, 721, 880, 1153, 1296, 1343, 1590, and 1765 cm^{-1}.

Butlar and Grebenshchikov[120] report the values 25 300 and 18 300 cm^{-1} for the $\nu_{S_1^*-S_0}$ and the ν_{T-S_0} transition frequencies respectively.

It should be noted that the S_1^* level is only 550 cm^{-1} lower, and the T level is actually 1500 cm^{-1} higher, than the corresponding levels in benzanthracene. Therefore, angular fusion of one additional ring leads to even closer approach of the energies of the S_1^* and T levels. The great similarity between the absorption curves of benzanthracene and dibenzanthracene is also noteworthy.

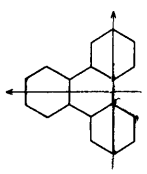
1,2;7,8-Dibenzonaphthacene (XII). Symmetry C_{2h}. Clar isolated p and β bands, having a coarse vibrational structure at room temperature, in the absorption spectrum of a benzene solution of this compound. The average interval is $\nu_{vibr} = 1400$ cm^{-1} for the p band. The structure of this band is very similar to those of naphthacene, benzonaphthacene, and dibenzonaphthacene. The initial ν_{00} band is quite strong (22 851 cm^{-1}), and has a higher frequency than the corresponding bands in naphthacene and benzonaphthacene. The fluorescence band[117] has three maxima: 23 000, 21 500, and 20 100 cm^{-1}. The T level is located at 18 000 cm^{-1}, i.e. 7300 cm^{-1} below the S_1^* level.

The absorption spectrum of 1,2; 8,9-dibenzopentacene in methylnaphthalene is reminiscent of the spectra of pentacene and benzopentacene, but this spectrum too occurs at shorter wavelengths than those of the last named hydrocarbons. The corresponding seven-ring linear polyacene is quite unstable. Less is known about the spectra of hydrocarbons having two benzene rings fused angularly to the polyacene chain symmetrically with respect to the short axis of the polyacene.

3,4-Benzophenanthrene (XIII) has a very unusual absorption spectrum with a 00 long-wavelength transition band (26 874 cm^{-1}) somewhat lower than in chrysene. The T level[119] is at 20 200 cm^{-1}, i.e. $\nu_{S_1^*-T} = 6700$ cm^{-1}.

The absorption spectrum of 1,2; 7,8-dibenzanthracene (XIV) has a very complex structure, beginning approximately at the same frequency ($\nu_{00} = 25\,309$) as that of 1,2; 5,6-dibenzanthracene. The energy[80] of the $T-S_0$ transition is approximately 17 900 cm^{-1}. The first phosphorescence band[78] is at 18 500 cm^{-1}, i.e. the T level lies 680 cm^{-1} below the S_1^* level (as in the case of 1,2;5,6-dibenzanthracene).

The absorption spectrum of 1,2; 9,10-dibenzonaphthacene (XV) has not been analysed in the literature. It consists of a large number of peaks; the long-wavelength peaks are similar to the absorption band of naphthacene; the first band is at 23 115 cm^{-1}, i.e. approximately at the same frequency as the absorption edge of 1,2;7,8-dibenzanthracene.



Triphenylene (XXXVI). Symmetry D_{3h}. Because of the presence of a third-order symmetry axis the electronic spectra of triphenylene show some specific features. The absorption spectrum has three bands: ^1L_b, ^1L_a, and ^1B_a (the ^1B_a and ^1B_b states are mixtures, as in benzene and coronene[85]). The electronic transitions ^1L_b and ^1L_a are forbidden by symmetry.

Butlar and Grebenshchikov[120] have recently obtained a quasi-linear structure for the $S_1^*-S_0$ and $T-S_0$ spectra in hexane and heptane solutions at 77°K. The 00 transition band at 29 138 cm^{-1}, coinciding in absorption and emission by resonance, was found to be very weak, in accordance with expectations that this band should be forbidden by symmetry. In the long-wavelength absorption spectrum the following vibrational differences were identified: 260, 606, 740, 1026, 1160, 1336, and 1416 cm^{-1}, of which the 1336 frequency is the one most frequently found in combination with other frequencies. The fluorescence spectrum contains more than 50 narrow bands, interpreted in terms of the fundamental frequencies 253, 616, 688, 749, 1048, 1185, 1341, 1430, and 1472 cm^{-1}.

The most characteristic frequency difference is 1341 cm^{-1}. The phosphorescence spectrum begins with a weak band ($\nu_{00} = 23\,587$ cm^{-1}), and has a very complicated structure. Only the differences 735, 1341, and 1430 cm^{-1} can be reliably identified. The polarisation phosphorescence spectrum has a vibrational structure[36].

1,2;3,4-Dibenzanthracene. Symmetry C_{2h}. The absorption spectrum in benzene begins with a weak α band at 3750 Å (26 660 cm^{-1}), which occurs at a shorter

wavelength than in the corresponding 1,2; 7,8- and 1,2; 5,6-isomers. The lower $S_1^*-S_0$ transition is close in energy to that of anthracene but the type of excitation of the electrons may be similar to that in chrysene and 1,2; 5,6- and 1,2; 7,8-dibenzanthracenes. The phosphorescence band has three maxima[78] at 17 770, 16 330, and 16 180 cm^{-1}.

1,2;3,4-Dibenzonapthacene. As the polyacene part of the molecule becomes longer, the electronic bands characteristic of the appropriate polyacene stand out more sharply. The long-wavelength absorption band of 1,2;3,4-dibenzonaphthacene is very similar in structure to the band in naphthacene. The same is true of the spectrum of 1,2;3,4-dibenzopentacene.

The fusion of four benzene nuclei to a polyacene produces a spectrum with a more complicated system of bands.

4. *peri*-FUSED HYDROCARBONS

In some cases it is more reasonable to regard *peri*-fused hydrocarbons as the result of the condensation not of simple benzene rings but of more complicated aromatic nuclei.

Pyrene (XVIII). Symmetry D_{2h}. This hydrocarbon can be regarded as the condensation product of two naphthalene rings. The absorption spectrum has four electronic bands: ^1L_b (ν_{00} = 26 900 cm^{-1}), ^1L_a (29 500 cm^{-1}), ^1B_b (36 400 cm^{-1}), and ^1B_a (41 300 cm^{-1}). Theoretical considerations predict polarisation of the ^1L_b and ^1B_b bands along the x axis, and polarisation of the ^1L_a and ^1B_a bands along the y axis. Measurements of polarised fluorescence by Williams[121] revealed that the polarisation is the same for the ^1L_b, ^1L_a, and ^1B_b bands. However, the polarisation spectra obtained by Zimmerman and Yoop[36] confirmed the theoretical predictions. The papers by Shpol'skii and his coworkers[44,45,55,118] describe studies of the structure of the electronic bands. Klimova[55] distinguished three systems of bands in absorption: a system of diffuse bands in the region 2800–2500 Å, a system of second electronic transition bands in the region 3400–3800 Å, and a system of $S_1^*-S_0$ transition bands in the region 3700–3400 Å.

Table 5, compiled from Ref. 55, illustrates the good agreement between the frequencies which are active in vibronic bands and the frequencies obtained from vibrational spectra (infrared and Raman). The possibility of interpreting the vibrational frequencies of the excited states of a molecule is also evident from Table 5.

The activity of vibration frequencies of type b_{1g} has been confirmed experimentally. Zimmerman and Yoop[36] distinguished two series of bands, polarised in mutually perpendicular directions, in the polarisation fluorescence spectrum of an alcoholic solution at -180°C. The main series began with a 00 band at ~26 900 cm^{-1}, and the origin of the second series was displaced towards lower frequencies by about 900 cm^{-1}. This difference is close to the frequency of the b_{1g} vibration ($\nu_{b_{1g}} \simeq$ 1106 cm^{-1}); the discrepancy between the observed frequencies arises from the inadequate resolution of the spectral structure in the alcohol solution.

The spectrum of the orange-red phosphorescence of the solutions is found in the region 16 900–15 250 cm^{-1}. The structure of the phosphorescence spectrum, interpreted using the frequencies 404, 1232, and 1406 cm^{-1}, is most sharply resolved at low temperatures in hexane solution[44,45,55]. The triplet level in the pyrene molecule lies 10 000 cm^{-1} below the S_1^* level ($\nu_{S_1^*-S_0} \simeq$ 26 837 cm^{-1}), so that the difference in the $\nu_{S_1^*-T}$ frequencies in pyrene is of the same order of magnitude as in the polyacenes. This fact provides evidence in favour of our suggestion regarding the condensation of naphthalene rings. Another surprising fact should be noted: the frequencies of the ^1L_b and ^1L_a 00 bands in the pyrene spectrum are lower than those of the corresponding bands in the naphthalene spectrum by approximately the same amount ($\Delta\nu\,^1L_b$ = 31 750 - 26 837 = = 4913 cm^{-1} and $\Delta\nu\,^1L_a$ = 34 500 - 29 500 = 5000 cm^{-1}). A decrease in the frequency of the ν_{00} bands of comparable magnitude is observed when the length of the polyacene chain is increased.

TABLE 5. Fundamental vibrational frequencies (cm^{-1}) of the pyrene molecule[55].

Second excited electronic state		First excited electronic state		Fluorescence spectrum		Raman spectrum		Infrared spectrum		Symmetry type
ν	intensity	ν	intensity	ν	intensity	ν	intensity	ν	intensity	
						349				
392	m.	392	m.	406		406	w.			a_g
454	w.	454	m.	456	m.			456	v.w.	b_{1u}
			s.	498	m.			497	m.	b_{3u}
			m.	559	w.	558	w.			
			m.	590	w.	591	m.	589	w.	a_g
			v.s.	678	w.			675	v.w.	
		722	m.	736	s.			734	m.	
786	w.	782	m.	802	s.					
				945	w.			945	v.w.	
				1028	w.					
				1068	m.	1067	w.			a_g
		1106	v.s.	1107	s.	1108	w.			b_{1g}
				1143	m.	1142	m.			a_g
1162	w.			1183	w.	1184	w.			a_g
1225	w.	1229	v.w.	1232	m.			1283	v.w.	
				1240	w.	1239	v.s.			a_g
						1308				
1327	m.			1325	m.	1327	v.w.			
						1349	w.			a_g
				1366	m.	1369	w.			b_{1g}
				1389	w.					
1393	w.	1394	w.	1405	v.s.	1407	v.s.			a_g
		1468	v.w.	1500	m.	1500	v.w.			
1500	m.	1528	v.w.	1551	m.	1551	v.w.			
				1595	m.	1594	s.			b_{1g}
				1631	m.	1631	v.s.			a_g
						2872	m.			
				3043	w.	3046	m.			b_{1g}

Note. m. = medium; w. = weak; s. = strong; v.s. = very strong; v.w. = very weak.

1,2-Benzopyrene (XIX). Symmetry C_{2v}. The absorption spectrum is fairly similar to that of pyrene in shape and position. Solutions have a violet fluorescence, with a band extending from 3750 to 4500 Å. At 77°K the fluorescence spectrum in alcohol splits into 10 bands, and the spectrum in hexane splits into ~100 bands. The relatively weak, first fluorescence band (ν_{00} = 26 570 cm^{-1}) is shifted towards the red by only 300 cm^{-1} as compared with the corresponding band of pyrene. Shpol'skii and coworkers[46] have given a detailed analysis of the fluorescence and phosphorescence spectra in hexane at 77° and 4°K. They identified 32 frequencies in the fluorescence bands, the most active of which are 1254, 1339, 1415, and 1444 cm^{-1}, assigned to fully symmetrical vibrations, and also 772 and 780 cm^{-1}, assigned to not fully symmetrical vibrations. The first four frequencies are intense only in

combination with the last two. The first phosphorescence band ν_{00} = 18 630 cm^{-1} is strong, and is separated from the ν_{00} fluorescence band by 7940 cm^{-1} (on the low-frequency side). Thus, the $\nu_{S_1^*-T}$ difference in 1,2-benzopyrene is lower than in pyrene. In the phosphorescence band, which extends over the region 5330–6700 Å, the following vibrational frequencies have been identified: 343, 383, 456, 649, 1090, 1150, 1255, 1262, 1339, 1415, and 1444 cm^{-1}. The absorption spectra of hydrocarbons consisting of a polyacene group fused to the pyrene nucleus in the 1,2-position can be treated as the sum of the absorption curves of pyrene and the corresponding polyacene. Thus, the long-wavelength absorption band of naphtho(2′, 3′-1,2)--pyrene is very similar in position and vibrational structure to the *P* band of anthracene. A second, very strong band, coincides with the strong β band of pyrene, and the third strong band coincides with the β band of anthracene. In a similar way, the absorption spectrum of 5,6; 15,16--dibenzohexacene can be described by superimposing the bands of naphthacene and pyrene.

3,4-Benzopyrene (XX). Symmetry C_{1h}. The fusion of a benzene ring to pyrene in the 3,4-position produces a more substantial change in the absorption spectrum than with 1,2-benzopyrene. The absorption spectrum begins with a stronger band, at a longer wavelength (4030 Å).

The bright fluorescence spectrum in alcohol and liquid paraffin solutions consists[122] of broad bands, spaced 1390 cm^{-1} apart. In hexane–octane solutions at 77°K these bands split into narrow-band multiplets[44]. Shpol'skii and Klimova[47] made a detailed analysis of the structure of the fluorescence band in heptance and other n-paraffins at 20° and 4°K. The strong component of the purely electronic multiplet is at 4023 Å (24 847 cm^{-1}); the following frequencies are active in the vibrational spectrum: 218, 335, 455, 613, 635, 853, 1111, 1163, 1237, 1345, 1389, 1417, 1586, and 1636 cm^{-1}. Frequency progressions by 1389 cm^{-1} are the most active, and give a characteristic periodicity to the spectrum. This is obviously associated with the same type of skeletal vibration as the 1406 cm^{-1} frequency in pyrene. The phosphorescence spectrum, which begins with a ν_{00} band at 14 670 cm^{-1}, has been described by Muel and Hubert-Habart[119], who report vibrational frequencies of 335 and 1237 cm^{-1}. Addition of a benzene ring to pyrene in the 3,4-position lowers the energies corresponding to $\nu_{S_1^*-S_0}$ and ν_{T-S_0} by the same amount (2000 cm^{-1}). It is surprising that the frequencies of these transitions in 3,4-benzopyrene are the same as in anthracene, despite the fact that the former has two additional benzene rings.

1,2; 4,5- or 3,4; 6,7-Dibenzopyrne (XXI). Symmetry C_{1h}. The absorption spectrum begins with a band at 4280 Å, and is similar to the spectrum of 3,4-benzopyrene, differing from it by a large number of weak, long--wavelength α bands. Although it is generally believed that the absorption spectrum begins at a longer wavelength than that of 3,4-benzopyrene, in fact, the purely electronic fluorescence bands show that the two spectra begin in the same region. A quasi-linear fluorescence spectrum (3900–4300 Å) in n-paraffins at 77°, 20°, and 4°K was obtained and analysed by Shpol'skii and Klimova[49,56]. The strongest component of the purely electronic multiplet in octane is at 25 250 cm^{-1}. 16 frequencies have been identified in the vibrational structure. Most of the fundamental frequencies coincide with those found to be active in the fluorescence spectrum of 3,4-benzopyrene: this follows, in part, from symmetry considerations (the two molecules have the same symmetry type). Fusion of a 6,7-ring to 3,4-benzopyrene produces an increase of ~400 cm^{-1} in the $\nu_{S_1^*-S_0}$ frequency. Unfortunately, there are no data on the position of the triplet level of this molecule. In the writer's opinion, the $\nu_{S_1^*-T}$ difference should decrease in the same way as on going from pyrene to 1,2-benzopyrene; the *T* level can be expected to lie in the region of 17 000 cm^{-1}.

3-Methyl-4,5-ethylene-3,4; 6,7-dibenzopyrene (XXII). The above hypothesis is confirmed by considering the spectra of 3-methyl-4,5-ethylene-3,4;6,7--dibenzopyrene (XXII), an alkyl derivative of the previous hydrocarbon. The structure of the long-wavelength absorption band and of the luminescence bands at 77°K in octane solution has been examined by Khesina[59,60]. Not surprisingly, the saturated five-membered ring and the methyl group produce a small bathochromic shift of the 00 band ($\nu_{S_1^*-S_0}$ 3988 Å, 25 065 cm^{-1}) as compared with 3,4; 6,7-dibenzopyrene. The following vibrational frequencies have been identified in the absorption band: 245, 270, 385, 440, 600, 635, 850, 1236, and 1415 cm^{-1}.

The fluorescence band contains the following frequencies: 251 (s.), 312 (m.), 410 (m.), 445 (s.), **602** (s.), 635 (s.), 854 (s.), 1236 (s.), **1354** (s.), 1415 (s.), and **1633** (s.). (These frequencies have similar values to the strong frequencies of 3,4; 6,7-dibenzopyrene.) The phosphorescence spectrum is shifted by 8600 cm^{-1} towards lower frequencies. It begins with a strong band at 6081 Å (16 450 cm^{-1}), and contains the differences 312 and 602 cm^{-1}, i.e. it occurs in the region which we have suggested for the phosphorescence of 3,4; 6,7-dibenzopyrene. Similar spectroscopic characteristics are to be expected also in another derivative of pyrene 1,2; 3,4-dibenzopyrene (XXIII), a close isomer of 3,4; 6,7-dibenzopyrene.

3,4-Naphtho-6,7-benzopyrene (XXV). Replacement of the benzene ring in the 3,4-position of 3,4; 6,7-dibenzopyrene by a naphthalene ring produces a decrease (to 23 900 cm^{-1}) in the frequency of the lower $S_1^*-S_0$ transition. Khesina[60] described the banded absorption, fluorescence, and phosphorescence spectra of a hexane solution of the compound at 77°K. The absorption spectrum was analysed from the ν_{00} band (23 917 cm^{-1}) in terms of the frequencies 190, 315, 471, 540, 745, 770, 990, 1370, 1430, and 1580 cm^{-1}, and the fluorescence spectrum in terms of the frequencies 205, **280**, **315**, **460**, **635**, 745, 785, 1340, 1440, and 1624 cm^{-1}. (These frequencies are active also in the phosphorescence spectrum.)

3,4,5,6,7-Tribenzopyrene. The frequencies of the $S_1^*-S_0$ and $T-S_0$ transitions in this molecule are not very different from the corresponding frequencies in 3-methyl-4,5-ethylene-3,4; 6,7-dibenzopyrene. The fluorescence band, located in the region 3950–5000 Å, splits (in octane solutions at 77°K) into a large number of narrow bands[60], interpreted in terms of the frequencies **286**, **387**, 415, 500, 690, 1267, 1311, 1410, and 1634 cm^{-1}. (These frequencies are active in the phosphorescence spectrum.) The first phosphorescence band (16 386 cm^{-1}) is separated from the first fluorescence band (25 258 cm^{-1}) by 8872 cm^{-1}. The frequencies 283, 385, 411, 620, and 645 cm^{-1} have been identified[59] in the long-wavelength absorption spectrum.

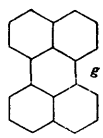
3,4; 8,9-Dibenzopyrne (XXVI). Symmetry C_{2h}. The absorption spectrum of a solution of this compound

begins with a 4510 Å band of medium intensity (a p band according to Clar); the second system extends from 3135 to 2400 Å. Shpol'skii and Klimova[49,56] analysed the structure of these bands in solutions of n-paraffins at 20° and 4°K. Six broad bands (3160–2900 Å) were detected in the region of the second transition. The long-wavelength absorption band with ν_{00} = 22 465 cm^{-1} was interpreted in terms of 17 frequencies, identical in value to frequencies which are active in the fluorescence spectrum. The fluorescence spectrum was interpreted in terms of 19 frequencies: 265 (v.s.), 419 (w.), 508 (w.), 647 (m.), 783 (v.w.), 1096 (w.), 1162 (m.), 1198 (s.), 1241 (v.s.), 1276 (s.), 1332 (w.), 1341 (w.), 1359 (v.w.), 1386 (s.), 1436 (s.), 1567 (m.), and 1632 (w.). The phosphorescence spectrum is shifted 10 425 cm^{-1} towards lower frequencies with respect to the fluorescence spectrum. According to Muel and Hubert-Habart[119] the 00 phosphorescence band is at 12 040 cm^{-1} in toluene, and there are vibrational differences of 280, 1400, and 2610 cm^{-1}. The 3,4; 8,9-dibenzopyrene molecule, like the anthanthrene molecule, can be regarded as the condensation product of two anthracene rings. The large energy difference between the S and T levels is retained, and the frequencies of the S_1^*–S_0 and T–S_0 transitions are close to the corresponding values for anthracene; $\nu_{S_1^*-S_0}$ is lower by about 3800 cm^{-1} than in anthracene and by about 2400 cm^{-1} than in 3,4-benzopyrene.

The absorption spectra of the other pyrene derivatives described in a series of papers by Clar[74–77] vary in a complicated manner with the number and positions of fused benzene rings.

Anthanthrene (XXVII). Symmetry C_{2h}. This molecule can be regarded as the result of the linear cyclisation of naphthalene or anthracene nuclei. The absorption spectrum contains three intense systems of bands: p, β, and β', according to Clar, beginning at 4330 Å (23 100 cm^{-1}). At room temperature[117] the fluorescence band has two maxima: 23 250 and 21 900 cm^{-1} ($\Delta\nu$ = 1350). In the phosphorescence spectrum, 5 bands have been identified. The first is at 11 850 cm^{-1}, the others are separated from it by 360, 740, 1430, and 1650 cm^{-1} respectively[119]. The difference in energies and levels is 11 400 cm^{-1}, i.e. of the same order as in the polyacenes.

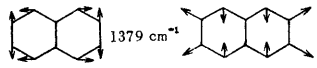
A different mode of condensation of aromatic rings is found in the perylene series.



Perylene. Symmetry D_{2h}. Perylene is readily prepared from naphthalene[73] by *peri*-condensation of naphthalene nuclei. The nuclei retain the π-electron conjugation of naphthalene, because the g bonds are not very different in length from single bonds. However, the absorption properties are vastly different. The frequency of the S_1^*–S_0 transition in perylene is lower than in naphthalene by 9000 cm^{-1}: this shift is greater than for the change from naphthalene to pyrene. The absorption spectrum is characterised by four bands: p, α, α', and β, according to Clar, with 00 transitions at the frequencies 22 700, 29 500, 34 300, and 39 600 cm^{-1} for an alcoholic solution[36] at -180°C (Clar gives[73] 22 800, 29 600, 34 300, and 39 000 cm^{-1}). Platt[84] made a theoretical study of the electronic states of perylene. His calculations gave transition energies different from the experimental values, with identical polarisations for the first three transitions.

The polarisation measurements of Williams[121], and Zimmerman and Yoop[36] showed that the 22 800 and 39 900 cm^{-1} transitions are polarised in mutually perpendicular directions. Hochstrasser[123] concluded that the long-wavelength transition is polarised along the long axis. The quasi-linear structure of the long-wavelength absorption and fluorescence bands (associated with an A_{1g}–B_{2u} transition) in hexane solution at 77°K has been described by Shpol'skii and Personov[48,58]. (The fluorescence spectrum under those same conditions was obtained earlier by Bowen and Brocklehurst[70].)

The strongest component of the multiplet of the purely electronic fluorescence band is at 4454 Å (22 445 cm^{-1}). The absorption bands have been analysed in terms of the frequencies 356, 420, 548, 1290, 1402, and 1604 cm^{-1}, and the fluorescence bands in terms of the frequencies 358, 430, 550, 1298, 1375, and 1578 cm^{-1}. In his analysis of these spectra, Personov[48,57] pointed out the identity of the frequencies of fully symmetrical vibrations which are active in the fluorescence spectra of naphthalene and perylene: 1379 and 1579 cm^{-1}. In the case of naphthalene these frequencies are associated with skeletal vibrations:



According to a calculation[80], the triplet level, or more accurately the frequency of the T–S_0 transition, lies in the region of 12 600 cm^{-1}. The difference between $\nu_{S_1^*-S_0}$ and ν_{T-S_0} amounts to 10 100 cm^{-1}, and is thus comparable in magnitude to the value for linear polyacenes. This is in keeping with the view that perylene is the result of *peri*-fusion of two naphthalene rings.

1,12-Benzoperylene (XXXIV). Symmetry C_{2v}. Since its structure is intermediate between those of perylene and coronene, 1,12-benzoperylene shows significant differences in spectral characteristics from these hydrocarbons. It would seem that addition of a benzene ring to perylene should induce, most probably, a bathochromic shift of the p band. However, although the absorption spectrum begins at λ_{00} = 4065 Å, i.e. at a longer wavelength than in perylene, this absorption is associated[73] with a weak α band ($\log\epsilon$ = 2.7). The stronger p band ($\log\epsilon$ = = 4–4.5) lies in the region 3900–3300 Å, and lastly the strongest β band lies in the region of 3000 Å. Ganguly and Mukherjee[124] measured the polarisation of the absorption bands for a single crystal, and showed that the p band is polarised along the long, y axis of the molecule. For the α band, they obtained the ratio I_b/I_a = 1.04, whereas a ratio of 0.015 is expected theoretically for polarisation along the axis. Nevertheless, the electronic transition of the long-wavelength band appears to be polarised along the x axis, and the discrepancy is due to the fact that the band structure is not resolved and contains overlapping vibrational bands polarised at right angles to each other, as in the absorption spectrum of phenanthrene[71] which has the same symmetry as that of 1,12-benzoperylene. Personov[58] was able to resolve and to interpret partly the complex vibrational structure of the long-wavelength absorption, fluorescence, and phosphorescence spectrum in paraffin solutions at 77°K. The 00 fluorescence band in hexane at 4060 Å (24 625 cm^{-1}) is fairly strong. The short-wavelength doublet at 16 258/16 228 cm^{-1} in the phosphorescence

spectrum is separated from the ν_{00} fluorescence band by 8400 cm^{-1}. The decrease in $\nu_{S_1^*-T}$ as compared with perylene and the occurrence of the long-wavelength α band are additional evidence of the similarity of the spectral properties of 1,12-benzoperylene and phenanthrene: 1,12-benzoperylene can be regarded as a dimer of phenanthrene. The dimerisation is accompanied by a decrease in the frequencies of the $S_1^*-S_0$ and $T-S_0$ transitions by 4200 and 5350 cm^{-1} respectively.

Comparison of 1,12-benzoperylene with phenanthrene allows us to understand the difference between its spectra and those of perylene, whose electronic states have peculiarities similar to those of the polyacenes.

Terrylene (XXIX). Symmetry D_{2h}. The *peri*-fusion of three naphthalene nuclei shifts the origin of the absorption spectrum towards longer wavelengths. The first band (5300 Å, 18 860 cm^{-1}) is 4000 cm^{-1} below that of perylene.

1,2-Benzoperylene. The absorption curve is similar to that of perylene, but shifted towards the long-wavelength region (first band at 5140 Å). A similar state of affairs is found with **1,2; 7,8-dibenzoperylene.** The origin of the absorption spectrum lies at still longer wavelengths (λ_{00} = 5460 Å). The spectrum of **1,2; 11,12-dibenzoperylene** is characterised by an even larger shift. The first absorption band is at 5580 Å (17 920 cm^{-1}).

In *meso*-naphthodianthrene (XXX) two anthracene nuclei are joined by three bonds in the *peri*-position. The long-wavelength absorption band is at 6625 Å (15 090 cm^{-1}). The frequency of the $S_1^*-S_0$ transition is 10 000 cm^{-1} lower than in anthracene, i.e. of the same order as on going from naphthalene to perylene.

1,14-bisanthene (XXXV). In this compound the initial λ_{00} band is at 6350 Å (15 740 cm^{-1}), 700 cm^{-1} higher than in *meso*-naphthodianthrene. The increase in the $\nu_{S_1^*-S_0}$ frequency is similar to that found in the spectra of the perylene–1,12-benzopyrene pair.

Coronene (XXXVII). This molecule has the same D_{6h} symmetry as the benzene molecule. This predetermines many of its general spectral properties. Three bands are distinguished in the absorption spectrum: ^1L_b, ^1L_a, and $^1B_{ab}$. Calculation showed that the $^1A-{}^1L_b$ and $^1A-{}^1L_a$ transitions are forbidden by symmetry, whereas the $^1A-{}^1B_{ab}$ transition is allowed. Mentzel and Zimmerman[38] gave a vibrational analysis of the absorption and luminescence bands of a solution of coronene in a mixture of tetrahydrofuran, alcohol, and ether (11 : 14 : 1) at 90°K. The structure of the $^1B_{ab}$ band (λ_{00} = 32 900 cm^{-1}) was analysed in terms of the differences 500, 1400, and 1700 cm^{-1}, the second frequency giving rise to the main series. The differences 500, 1000, 1200, 1350, and 1500 cm^{-1} were identified in the ^1L_a band, which extends from 28 850 to 32 400 cm^{-1}. The last two give rise to series. The ^1L_b band (ν_{00} = 23 500 cm^{-1}) was interpreted in terms of the frequencies 350, 650, 1250, 1350, 1450, and 1600 cm^{-1}. The series are determined by the frequencies 1350 and 1600 cm^{-1}. It has also been shown that the absorption bands of 1,12-benzoperylene, which is usually present as an impurity in coronene, appear in the spectrum. Bowen and Brocklehurst obtained a quasi-linear structure from the luminescence spectra of coronene in hexane at 77°K, and also noted the presence of the fluorescence bands of 1,12-benzoperylene, present as an impurity[70]. Shpol'skii and coworkers[44] published a detailed vibrational analysis of the fluorescence spectrum of coronene, which consists, in hexane at 77°K, of sharp doublets beginning at 23 543/23 456 cm^{-1}. These workers pointed out the active status of the "breathing" frequency of the benzene ring (992 cm^{-1}) and of the symmetrical stretching vibration of the C–H bonds (3070 cm^{-1}). Sidman[125] analysed the fluorescence spectrum in hexane at -180°C and assigned the 320 and 1400 cm^{-1} frequencies to vibrations of e_g^+ symmetry. Mentzel and Zimmerman[38] interpreted the fluorescence spectrum, consisting of 24 bands with an initial band at 23 500 cm^{-1}, in terms of the frequencies 350, 650, 1000, 1250, 1450, and 1600 cm^{-1}. They observed a constant polarisation along the entire fluorescence spectrum.

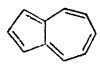
The phosphorescence spectrum of the compound in the crystalline state was studied at 77°K by Clar and Zander[78], in a mixture of propyl ether and isopentane at 90°K (ν_{00} = = 19 410 cm^{-1}) by Czekalla and Mager[103], in hexane and heptane at 77°K (ν_{00} = 19 375) by Shpol'skii and Klimova[50], and in alcohol at 90°K (ν_{00} = 19 400) by Dörr and Cropper[40]. A detailed analysis of the structure, using the best spectral resolution[50], led to the identification of the fundamental frequencies 120, 365, 850, 1157, 1226, 1350, 1405, 1435, 1618, and 1630 cm^{-1}. The polarisation phosphorescence spectrum shows a large change of polarisation along the spectrum[40]; this indicates the occurrence of not fully symmetrical vibrations whose frequencies, however, were not identified. It should be noted that in a mixed crystal with perhydrocoronene, delayed fluorescence (due to the return of the molecule from the T to the S_1^* state followed by $S_1^*-S_0$ radiation) is observed for coronene in addition to phosphorescence[23,126]. Zander[127] found that, on increasing the temperature, the relative intensity of the $T-S_0$ emission decreases, whilst the delayed fluorescence increases. So far coronene is the only hydrocarbon for which this type of delayed fluorescence has been observed. This is because the energy difference between the S_1^* and the T states is least in coronene: $\nu_{S_1^*-T}$ = 4100 cm^{-1}. Such a large drop in $\nu_{S_1^*-T}$ arises because in this molecule the angular cyclisation of benzene rings proceeds to a complete cycle.

The spectral features of fused polycyclic hydrocarbons containing a five-membered ring are discussed below using fluorene and fluoranthene as examples

Fluorene (XXXIX). Symmetry C_{2v}. The molecule has the π-electron system of the biphenyl nucleus, the $-CH_2-$ bridge affecting the energy of electronic transitions like an alkyl substituent. The long-wavelength $S_1^*-S_0$ transition is polarised, as in the biphenyl molecule, along the C–C bond linking the benzene rings[128]. There are papers giving an analysis of the vibrational structure of the long-wavelength absorption band of fluorene in the crystalline state[61,128] and in frozen solutions[61]. The resonance band in absorption and fluorescence is at 33 160 cm^{-1} (in heptane). The fluorescence band spectrum of the crystals has also been described; it has been shown[128] that the frequencies 404 and 564 cm^{-1} give rise to strong series of bands for fully symmetrical vibrations, polarised along the short axis of the molecule. Nurmukhametov and Gobov[61] described also the fluorescence and phosphorescence band spectram of a heptane solution at 77°K. The structure of the phosphorescence band of a cyclohexane solution of this compound has been described[69]. The purely electronic

phosphorescence band (23 786 cm^{-1}) lies 9374 cm^{-1} below the first fluorescence band.

Fluoranthene (XXXVIII). Quasi-linear luminescence spectra have been obtained by Val'dman and Sheremet'ev[129] at 77°K in heptane. The vibrational frequencies 226, 343, 556, 792, 908, and 1614 cm^{-1} in the blue fluorescence band were identified with ν_{00} = 24 521 cm^{-1}. The orange-red phosphorescence spectrum begins with a band at 18 416 cm^{-1} and contains the frequencies 343, 556, 792, 1175, 1310, 1420, and 1614 cm^{-1}. The difference between the S_1^* and the T levels is 6105 cm^{-1}; cyclisation of benzene rings around a five-membered ring lowers this difference, just as it does in the case of cyclisation around a benzene ring (triphenylene, coronene). Lastly, we shall consider the work on the structure of the spectrum of azulene, which consists of two condensed rings (one five-membered and one seven-membered).

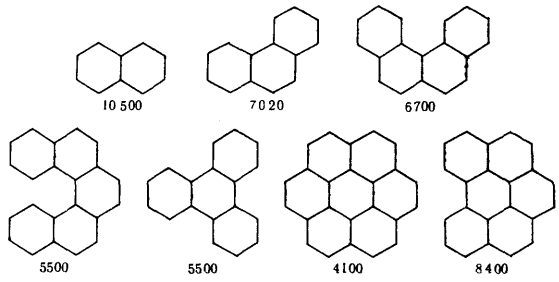


The hydrocarbon azulene has unusual properties: being coloured, it shows ultraviolet fluorescence[130-133]. It has been shown that the fluorescence is due to emission from the second excited singlet level, whereas excitation in the first absorption band does not cause luminescence[130]. Ruzevich[133] obtained a well resolved vibrational structure of the fluorescence band in hexane solution at 77°K.

---o0o---

We shall now consider the correlations which have been established empirically between the position and the structure of the electronic bands. An increase in the length of the π-electron system in the polyacene series (naphthalene, anthracene, naphthacene, pentacene, hexacene) causes a monotonic decrease in the energy of the long-wavelength $S_1^*-S_0$ and $T-S_0$ transitions by the following amounts: 5500 (6370 for ν_{T-S_0}), 5080 (4430), 4000 (2500), and 3000 cm^{-1}. As will be clear from the subsequent discussion, the decrement in $\nu_{S_1^*-S_0}$ and ν_{T-S_0} frequencies per benzene ring is largest in the polyacenes, with an average value of 5000 cm^{-1} for the first few members. All the polyacenes, beginning with anthracene, have a "*p* band", with a very similar coarse vibrational structure. This similarity arises because one of the frequencies in the region 1400 cm^{-1} is predominant. The difference in position between the S_1^* and T levels, amounting to some 10 000 cm^{-1}, is hardly affected by an increase in the number of condensed rings in the polyacene series (see Table 3). Molecules which can be regarded as formed by the condensation of more complicated aromatic nuclei also show this type of spectral peculiarity. Thus, the pyrene molecule is obtained by the linear condensation of two naphthalene nuclei, the molecule of anthanthrene can be derived from two anthracene or three naphthalene nuclei, and the molecule of 1,12-benzoperylene from two phenanthrene molecules. The energies of the $S_1^*-S_0$ and $T-S_0$ transitions in the spectra of the pairs of compounds naphthalene–pyrene, anthanthrene–anthracene, and 1,12-benzopyrene–phenanthrene differ by the following amounts respectively: 4900 (4400 for $T-S_0$), 3000 (3000), and 4200 (5550) cm^{-1}. Thus, fusion of the more complicated aromatic nuclei lowers the frequency of the electronic bands by about the same amount as in the polyacenes, despite the fact that the number of benzene rings in the molecule is increased by more than unity. The difference between the frequencies $\nu_{S_1^*-S_0}$ and ν_{T-S_0} also stays practically constant in condensation of this type: in pyrene and anthanthrene $\nu_{S_1^*-T}$ equals 9900 and 11 400 cm^{-1} respectively. *Peri*-condensation of naphthalene and anthracene nuclei (as in perylene) lowers the frequencies of the long-wavelength bands more significantly than in the pyrenes. However, this decrease is less than in the polyacenes when calculated for a single ring. Again, the frequency difference between $\nu_{S_1^*-S_0}$ and ν_{T-S_0} is found to be constant (in perylene $\nu_{S_1^*-T}$ = 10 000 cm^{-1}). When π-electron groups are conjugated in an open chain, as in the polyphenyls and diphenylpolyenes, the decrease in $\nu_{S_1^*-S_0}$ frequency per unit of the conjugated system is smaller than in the polyacenes by about a factor of two. In these classes of compounds, phosphorescence has been observed only for biphenyl, in the spectrum of which the $\nu_{S_1^*-T}$ difference amounts to 10 000 cm^{-1}.

A different type of spectral changes is observed for angularly condensed hydrocarbons. Fusion of a benzene ring to a polyacene molecule in the 1,2-position causes a much smaller shift of the long-wavelength origin of the absorption spectrum. The α bands are more affected than the p bands, which keep their position unchanged in the benzopolyacene series. As a result, the α band becomes the long-wavelength band in some benzopolyacenes instead of the p band (the long-wavelength band in the corresponding polyacenes). In benzopolyacenes with a long polyacene chain the shift is insufficient, and the p band retains the long-wavelength position and is very similar to the p band of the polyacene. Also, angular condensation decreases the difference between the S_1^* and T levels: in phenanthrene this difference drops to 7080 cm^{-1}, in benzanthracene to 9500 cm^{-1}. Angular fusion of two or more benzene rings to the end rings of polyacenes increases the tendencies noted for the monobenzopolyacenes. In 3,4-benzophenanthrene the difference drops to 6700 cm^{-1}, in triphenylene to 5500 cm^{-1}. The maximum degree of angular cyclisation occurs in coronene, and this coincides, characteristically, with a minimum value of the difference $\nu_{S_1^*-T}$ (4100 cm^{-1}). The decrease in the difference $\nu_{S_1^*-T}$ is clearly illustrated by the series



It must be emphasised that 1,12-benzoperylene is not included in this series because it is regarded as the result of the linear condensation of two phenanthrene molecules.

Essentially, this series spans the whole range of $\nu_{S_1^*-T}$ values met in aromatic hydrocarbons (from 12 000 to 4000 cm^{-1}). The rule relating the relative positions of the S_1^* and T levels to the structure of the π-electron system of the molecule enables us to predict the region in which the phosphorescence spectrum of aromatic hydrocarbon molecules can be expected to occur from a knowledge of the absorption or fluorescence spectrum. A knowledge of the position of the S and T levels and of the

absorption and luminescence spectra of aromatic hydrocarbons as a function of molecular structure is valuable from many points of view. Several of these compounds show photochemical activity, being particularly susceptible to photo-oxidation. The majority of the reactions proceed through a metastable triplet state. Zander[134] pointed out that a hydrocarbon becomes more and more unstable as the energy of the triplet level drops. Pentacene and hexacene react almost like free radicals. Hexacene is readily oxidised, and reacts instantaneously with maleic anhydride, which decolourises it. Octacene and nonacene appear to be true biradicals. The higher relative position of the T level in angularly condensed hydrocarbons accounts for their high stability as compared with the acenes containing the same number of benzene rings. Many hydrocarbons form photo-oxides under illumination in the presence of oxygen. Using the well-known photo-oxidation of anthracene solutions as an example, it was shown[135] that formation of the photo-oxide involves the participation of a T state. In view of published statements that the T states of organic molecules are promising routes to the realisation of efficient lasers[136,137], it may be useful to assess the possibilities offered by aromatic hydrocarbons. On the whole, these compounds are not very promising. The phosphorescence of all the hydrocarbons examined is characterised by glow-decay times between 0.1 and a few seconds. Most of them have triplet–triplet absorption bands overlapping the absorption spectrum of the S_1^*–S_0 transitions. The phosphorescence yield is no more than one-half of the luminescence yield. Lastly, the Stokes losses during excitation are large.

Many aromatic hydrocarbons show carcinogenic properties, which were originally ascribed to the luminescence of these materials but are now regarded as being associated with the position of the levels. Muel and Hubert-Habart[119] found no unique correlation between the position of the T level and the carcinogenic activity of aromatic hydrocarbons. Attempts have also been made to correlate carcinogenic action with the electron donor or acceptor properties of the molecules[138], again without real success. This property of the molecules does not appear to be determined by a single molecular parameter, but rather by a combination of parameters.

1. L.D. Landau and E.M. Lifshits, "Kvantovaya Mekhanika" (Quantum Mechanics), GITTL, Moscow, 1948.
2. M.A. El'yashevich, "Atomnaya i Molekulyarnaya Spektroskopiya" (Atomic and Molecular Spectroscopy), Moscow, 1962.
3. G. Herzberg, "Molecular Spectra and Molecular Structure. Vol. 1. Spectra of Diatomic Molecules" (Translated into Russian), Inostr. Lit., Moscow, 1949.
4. G. Herzberg, "Molecular Spectra and Molecular Structure. Vol. 2. Infrared and Raman Spectra of Polyatomic Molecules" (Translated into Russian), Inostr. Lit., 1949.
5. A.N. Terenin, "Fotokhimiya Krasitelei i Rodstvennykh Organicheskikh Soedinenii" (Photochemistry of Dyes and Related Organic Compounds), Izd. Akad. Nauk SSSR, Moscow, 1947.
6. H.H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy", New York, 1962.
7. H. Sponer and E. Teller, "Electronic Spectra of Polyatomic Molecules", Rev. Mod. Phys., 13, 76 (1941).
8. V. Heine, "Group Theory in Quantum Mechanics" (Translated into Russian), Inostr. Lit., 1963.
9. S. Bhagavantam and T. Venkatarayudu, "Theory of Groups and Its Application to Physical Problems" (Translated into Russian), Inostr. Lit., 1959.
10. B.A. Tavger, Optika i Spektrosk., 15, 561 (1963).
11. A.V. Karyakin and V.N. Duzhenkov, Uspekhi Khim., 31, 1511 (1962) [Russ. Chem. Rev., 721 (1962)].
12. A.N. Terenin, Zhur. Fiz. Khim., 18, 1 (1944).
13. G.N. Lewis and M. Kasha, J. Amer. Chem. Soc., 66, 2100 (1944); 67, 994 (1945).
14. G.N. Lewis and M. Calvin, J. Amer. Chem. Soc., 67, 1232 (1945); G.N. Lewis, M. Calvin, and M. Kasha, J. Chem. Phys., 17, 804 (1949).
15. D.F. Evans, Nature, 176, 777 (1955).
16. C.A. Hutchison and B.W. Mangum, J. Chem. Phys., 29, 952 (1958).
17. J.H. Waals and M.S. Groot, Mol. Phys., 3, 190 (1960); 2, 333 (1959).
18. A.K. Piskunov, R.N. Nurmukhametov, D.N. Shigorin, V.I. Muromtsev, and G.A. Ozerova, Izv. Akad. Nauk SSSR, Ser. Fiz., 27, 634 (1963).
19. I.V. Obreimov and A.F. Prikhot'ko, Phys. Z. Sowjetunion, 9, 34, 48 (1936).
20. A.F. Prikhot'ko, Optika i Spektrost., 3, 484 (1957).
21. D.S. McClure, J. Chem. Phys., 22, 1668 (1954); 24, 1 (1956).
22. D.S. McClure, J. Chem. Phys., 25, 481 (1956).
23. J.W. Sidman, Phys. Rev., 102, 96 (1956).
24. J.W. Sidman, J. Chem. Phys., 25, 115 (1956).
25. J.W. Sidman, J. Chem. Phys., 25, 122 (1956).
26. P. Pesteil, Ann. Physique, [12], 10, 128 (1955).
27. B. Stevens, Spectrochim. Acta, 18, 439 (1962).
28. T. Förster and K. Kasper, Z. phys. Chem. (Frankfurt), 1, 275 (1954).
29. T. Förster and K. Kasper, Z. Elektrochem., 59, 977 (1955).
30. E. Döller and T. Förster, Z. phys. Chem. (Frankfurt), 34, 132 (1962).
31. T. Förster, Pure Appl. Chem., 7, 73 (1963).
32. H. Zimmerman and N. Yoop, Z. Elektrochem., 64, 1215 (1960).
33. H. Zimmerman and N. Yoop, Z. Elektrochem., 64, 1219 (1960).
34. H. Zimmerman and N. Yoop, Z. Elektrochem., 65, 61 (1961).
35. H. Zimmerman and N. Yoop, Z. Elektrochem., 65, 66 (1961).
36. H. Zimmerman and N. Yoop, Z. Elektrochem., 65, 138 (1961).
37. H. Zimmerman and N. Yoop, Z. Elektrochem., 67, 342 (1962).
38. N. Mentzel and H. Zimmerman, Z. Elektrochem., 67, 582 (1963).
39. H. Cropper and F. Dörr, Z. Elektrochem., 67, 46 (1963).
40. F. Dörr and H. Cropper, Z. Elektrochem., 67, 193 (1963).
41. R. Müller and F. Dörr, Z. Elektrochem., 63, 1150 (1959).
42. E.V. Shpol'skii, A.A. Il'ina, and L.A. Klimova, Dokl. Akad. Nauk SSSR, 87, 935 (1952).
43. E.V. Shpol'skii, Uspekhi Fiz. Nauk, 68, 51 (1959); 71, 215 (1960); 80, 255 (1963).
44. E.V. Shpol'skii, E.A. Girdzhiyauskaite, and L.A. Klimova, "Materialy X Vsesoyuznogo Soveshchaniya po Spektroskopii" (Proceedings of the Tenth All-Union Conference on Spectroscopy), Lvov, 1957, Vol. 1, p. 24.
45. E.V. Shpol'skii and E.A. Girdzhiyauskaite, Optika i Spektrosk., 4, 20 (1958).
46. E.V. Shpol'skii, L.A. Klimova, and R.I. Personov, Optika i Spektrosk., 13, 341 (1962).
47. E.V. Shpol'skii and L.A. Klimova, Optika i Spektrosk., 13, 174 (1962).
48. E.V. Shpol'skii and R.I. Personov, Optika i Spektrosk., 8, 328 (1960).

49. E.V. Shpol'skii and L.A. Klimova, "Sbornik, Fizicheskie Problemy Spektroskopii" (Physical Problems in Spectroscopy), 1962, Vol.I, p.209.
50. E.V. Shpol'skii and L.A. Klimova, Izv. Akad. Nauk SSSR, Ser. Fiz., 23, 23 (1959).
51. T.N. Bolotnikova, Optika i Spektrosk., 7, 44, 217 (1959).
52. T.N. Bolotnikova, Izv. Akad. Nauk SSSR, Ser. Fiz., 23, 29 (1959).
53. T.N. Bolotnikova, Candidate's Thesis, Lenin Moscow State Pedagogic Institute, 1959.
54. E.A. Girdzhiyauskaite, Candidate's Thesis, Lenin Moscow State Pedagogic Institute, 1958.
55. L.A. Klimova, Optika i Spektrosk., 15, 344 (1963).
56. L.A. Klimova, Candidate's Thesis, Lenin Moscow State Pedagogic Institute, 1963.
57. R.I. Personov, Izv. Akad. Nauk SSSR, Ser. Fiz., 24, 620 (1960).
58. R.I. Personov, Candidate's Thesis, Lenin Moscow State Pedagogic Institute, 1963.
59. A.Ya. Khesina, Izv. Akad. Nauk SSSR, Ser. Fiz., 24, 623 (1960).
60. A.Ya. Khesina, Optika i Spektrosk., 10, 607 (1961).
61. R.N. Nurmukhametov and G.V. Gobov, Optika i Spektrosk., 13, 676 (1962).
62. R.N. Nurmukhametov and E.G. Popova, "Fizicheskie Problemy Spektroskopii, Materialy 13-go Soveshchaniya" (Physical Problems in Spectroscopy, Academy of Sciences of the USSR, Materials of the 13th Conference, Leningrad, 4th–12th July 1960), Izd. Akad. Nauk SSSR, 1962, Vol. 1, p.216.
63. R.N. Nurmukhametov, Candidate's Thesis, Lenin Moscow State Pedagogic Institute, 1962.
64. R.N. Nurmukhametov, E.G. Popova, and N.S. Dokunikhin, Optika i Spektrosk., 9, 593 (1960); 11, 134 (1961).
65. P.A. Teplyakov, Optika i Spektrosk., 15, 645 (1963).
66. V.L. Levshin and Kh.I. Mamedov, Optika i Spektrosk., 12, 593 (1962).
67. H. Sponer, Y. Kanda, and L. Blackwell, Spectrochim. Acta, 16, 1135 (1960).
68. Y. Kanda and R. Shimada, Spectrochim. Acta, 17, 279 (1961).
69. Y. Kanda and R. Shimada, Spectrochim. Acta, 17, 1278 (1961).
70. E.Y. Bowen and B. Brocklehurst, J. Chem. Soc., 3875 (1954); 4320 (1955).
71. P. Pesteil and M. Rabaud, J. Chim. phys., 59, 167 (1962).
72. E.B. Clar, Spectrochim. Acta, 4, 116 (1950).
73. E.B. Clar, "Aromatische Kohlenwasserstoffe", Berlin, 1952.
74. E.B. Clar, Z. Chem., 2, 35 (1962).
75. E.B. Clar, Y.F. Guye-Vuilleme, S. McCallum, and J.A. Macpherson, Tetrahedron, 19, 2185 (1963).
76. E.B. Clar, S. McCallum, and R.A. Robertson, Tetrahedron, 18, 1471 (1962).
77. E.B. Clar and M. Zander, Tetrahedron, 19, 521 (1963).
78. E.B. Clar and M. Zander, Chem. Ber., 89, 749 (1956).
79. C. Reid, J. Chem. Phys., 20, 1214 (1952).
80. G.G. Hall, Proc. Roy. Soc., A 213, 113 (1952); Trans. Faraday Soc., 53, 573 (1957).
81. H.B. Klevens and J.R. Platt, J. Chem. Phys., 17, 470 (1949).
82. J.R. Platt, J. Chem. Phys., 17, 484 (1949).
83. J R. Platt, J. Chem. Phys., 18, 1168 (1950).
84. J.R. Platt, J. Chem. Phys., 22, 1148 (1954).
85. N.S. Ham and K. Ruedenberg, J. Chem. Phys., 25, 13 (1956).
86. R. Pariser, J. Chem. Phys., 24, 250 (1956).
87. W. Moffit, J. Chem. Phys., 22, 320 (1955).
88. T. Handa, Bull. Chem. Soc. Japan, 36, 325 (1963).
89. A.H. Hilmer and E. Paersch, Z. phys. Chem., A 161, 46 (1932).
90. V.L. Braude, Uspekhi Fiz. Nauk, 74, 577 (1961).
91. H. Sponer, G. Nordheim, A.L. Sklar, and E. Teller, J. Chem. Phys., 7, 207 (1939).
92. C. Coupron, R. Lochet, Y. Meyer, and A. Rousset, Compt. rend., 250, 3095 (1960).
93. H. Shull, J. Chem. Phys., 17, 295 (1949).
94. P.P. Dikun and B.Ya. Sveshnikov, Dokl. Akad. Nauk SSSR, 65, 637 (1949); Zhur. Eksper. Teor. Fiz., 19, 1000 (1949).
95. D.P. Craig, Y.M. Hollas, M.F. Redies, and S.K. Wait, Proc. Chem. Soc., 361 (1959).
96. O. Schepp and D.S. McGlure, J. Chem. Phys., 20, 1975 (1952); Bull. Amer. Phys. Soc., 26, 27 (1951).
97. D.E. Freeman, J. Mol. Spectroscopy, 6, 305 (1961).
98. Y.M. Hollas, J. Mol. Spectroscopy, 9, 138 (1962).
99. H. Luther and H.J. Drewitz, Z. Elektrochem., 66, 546 (1962).
100. N.I. Zhirnov, Optika i Spektrosk., 9, 734 (1960).
101. M.A. Kovner and E.P. Krainov, Optika i Spektrosk., 15, 565 (1963).
102. Y. Czekalla, G. Briegleb, W. Herre, and H.Y. Vahlensieck, Z. Elektrochem.. 63, 715 (1959).
103. Y. Czekalla and K.Y. Mager, Z. Elektrochem., 66, 65 (1962).
104. K.R. Popov, Optika i Spektrosk., 3, 579 (1957).
105. D.P. Craig and P.C. Hobbins, J. Chem. Soc., 539, 2302 (1955).
106. R.N. Jones and E. Spinner, Spectrochim. Acta, 16, 1060 (1960).
107. S.P. McGlynn, J.D. Boggus, and E. Elder, J. Chem. Phys., 32, No. 2 (1960).
108. O.P. Kharitonova, Optika i Spektrosk., 5, 30 (1958).
109. Y. Kanda and R. Shimada, Spectrochim. Acta, 16, 1060 (1960).
110. Y.L. Patenaude, P. Sauvageau, and C. Sandorfy, Spectrochim. Acta, 18, 241 (1962).
111. C. Sandorfy and R.N. Jones, Canad. J. Chem., 34, 888 (1957).
112. R. Schoental and E.Y. Scott, J. Chem. Soc., 1683 (1949).
113. M.M. Moodie and C. Reid, J. Chem. Phys., 22, 252 (1954).
114. M. Kasha, Chem. Rev., 41, 401 (1947).
115. J.B. Birks and A.J.W. Cameron, Proc. Roy. Soc., A 249, 297 (1959).
116. A. Rousset, R. Lochet, and J.L. Dubarry, Compt. rend., 248, 54 (1959).
117. R. Schoental and E.J.Y. Scott, J. Chem. Soc., 1683 (1949).
118. A.A. Il'ina and E.V. Shpol'skii, Izv. Akad. Nauk SSSR, Ser. Fiz., 15, 585 (1951).
119. B. Muel and M. Hubert-Habart, J. Chim. phys., 55, 377 (1958).
120. V.A. Butlar and D.M. Grebenshchikov, "Trudy I Mezhvuzovskoi Konferentsii po Radiofizike i Spektroskopii" (Proceedings of the First Intercollegiate Conference on Radiation Physics and Spectroscopy), Moscow, 1964.
121. R.W. Williams, J. Chem. Phys., 26, 1186 (1957).
122. E.V. Shpol'skii and A.A. Il'ina, Zhur. Eksper. Teor. Fiz., 21, 142 (1951).
123. R.M. Hochstrasser, Canad. J. Chem., 39, 451 (1961).
124. S.C. Ganguly and B.C. Mukherjee, Proc. Phys. Soc., 79, 220 (1962).
125. J.W. Sidman, J. Chem. Phys., 23, 1365 (1955).
126. L. Boente, Brennstoff-Chem., 36, 211 (1955).
127. M. Zander, Naturwiss., 47, 443 (1960).
128. P. Pesteil and M. Barbaron, Compt. rend., 238, 75, 1400 (1954).
129. M.M. Val'dman and G.D. Sheremet'ev, "Trudy Fiziko-Matematicheskogo Fakul'teta Chelyabinskogo Pedagogicheskogo Instituta" (Transactions of the Physical and Mathematical Faculty of the Chelyabinsk Pedagogic Institute), 1964, Vol. 2.

130. M. Beer and H. C. Longuet-Higgins, J. Chem. Phys., 23, 1390 (1955).
131. C. Visvanath and M. Kasha, J. Chem. Phys., 24, 574 (1956).
132. J. W. Sidman and D. M. McGlure, J. Chem. Phys., 24, 757 (1956).
133. Z. S. Ruzevich, Optika i Spektrosk., 15, 357 (1963).
134. M. Zander, Angew.Chem., 72, 513 (1960).
135. A. S. Cherkasov and T. M. Vember, Optika i Spektrosk., 6, 503 (1959).
136. E. G. Brock, P. Csavinszky, E. Hormats, H. S. Nedderman, D. Stirpe, and E. Untereither, J. Chem. Phys., 35, 759 (1961).
137. D. J. Morantz, B. G. White, and J. E. Wright, J. Chem. Phys., 37, 2041 (1962).
138. B. Pullman, A. Pullman, A. C. Allison, and T. Nash, Nature, 199, 467 (1963).

Karpov Moscow Physicochemical Institute