

BORAZARO ANALOGUES OF AROMATIC HYDROCARBONS. I. ELECTRONIC SPECTRA

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Dedicated to the 65th anniversary of the late Academician R. Brdička.

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Room- and low-temperature ultraviolet absorption spectra and low-temperature emission spectra of seven borazaro analogues of naphthalene, phenanthrene, and triphenylene are reported, and compared with the spectra of the parent hydrocarbons. In most cases, numerous individual electronic transitions can be discerned.

Heterocyclic analogues of aromatic hydrocarbons containing a boron and nitrogen atom in adjacent positions have now been studied for some time, most intensely by Dewar and co-workers^{1,2}. In spite of the interest that these cross-breeds of benzene and borazine³ have aroused, surprisingly little is known about their electronic spectra. A qualitative discussion of basic features of the spectra of several such compounds has been given by Dewar². A more detailed study of these properties might provide more information about just how similar these compounds are to the parent hydrocarbons. Indeed, the similarity of the UV absorption curves of these heterocycles and the parent hydrocarbons is one of the reasons why they have been considered aromatic². Furthermore, an improved knowledge of electronically excited states might provide a solid background for the application of semiempirical quantum chemical theories, which depend on fitting of parameters to well-understood experimental data. Thus, it might become possible to predict some of the properties of as yet unknown members of this interesting class of compounds.

The present paper reports an investigation of the electronic spectra of molecules *I–VII*; a following paper⁴ presents results of semiempirical calculations.

EXPERIMENTAL

Chemicals. The samples originated from collections of Prof. M. J. S. Dewar, Chemistry Department, University of Texas at Austin. They were purified by sublimation and where required also by crystallization and had the following melting points: *I*: 73–73.5°C, *II*: 49–50°C, *III*: 97–97.5°C, *IV*: 99.5–100.5°C, *V*: 74–75°C, *VI*: 181–182°C, *VII*: 196.5°C. 3-Methylpentane (Phillips Petroleum Co.) was dried and distilled before use.

Spectral measurements. Dichroic spectra of *II* in stretched polyethylene sheet at 77°K were measured using an apparatus to be described elsewhere⁵. Absorption spectra were taken on a Cary 15

instrument. A quartz Dewar vessel with flat windows was used for work at 77°K. Emission spectra were recorded in the front surface arrangement using a 1 kW xenon arc, a 250 mm Bausch and Lomb monochromator for exciting light and an Aminco scanning monochromator (slits 0.05–0.50 mm) for emitted light, and were corrected for photomultiplier response. They were independent of the choice of excitation wavelength. The resolution is lower than that in absorption work. Excitation spectra were recorded in each case and compared well with absorption spectra. The origin of fluorescence coincided within 500 cm^{-1} with the origin of absorption. In two cases (*I* and *VI*) very weak ($\epsilon = 5 - 30$) additional absorption was noticed on the long-wavelength side of the origins; it was assigned to traces of impurities. All absorption and emission measurements were repeated several times using varying concentrations, slitwidths, and excitation wavelengths to bring out maximum spectral detail. Typical concentrations used in the emission work were $10^{-3} - 10^{-4}\text{ M}$. In several cases strong phosphorescence was noticed. No effort to study it in detail was made but positions of 0–0 components shall be listed.

RESULTS

Absorption spectra at 77° and 298°K and fluorescence spectra at 77°K are shown in Figs 1, 2, and 4–8. Fig. 3 presents the dichroic spectrum of *II* in stretched polyethylene.

The spectra show considerable fine structure reminiscent of the parent hydrocarbons. In most cases, the fine structure is quite regular. Unfortunately, an analysis is severely hampered by the low resolution available. Although we realize this inherent limitation we have attempted to rationalize the observed regularities in terms of a minimum number of active vibrational frequencies whenever possible, guided by analogy with cases such as the parent hydrocarbons in which fine structure is better understood from high-resolution studies. It is possible that some of the suggested progressions in one vibration are in reality unresolved progressions in two or more vibrations of similar frequencies as suggested by the frequently observed gradual broadening of the higher members of the progression.

We have attempted to postulate as few independent electronic transitions as reasonably possible and most problematic peaks were assigned as members of progressions whose first or last members are too weak to be resolved rather than as due to new transitions. In addition to the regularities in the fine structure, the following features were considered in postulating the presence of an independent electronic transition: band shapes and intensities, temperature shifts, approximate mirror image symmetry between fluorescence spectrum and the first band in the absorption spectrum, and, in some cases, obvious similarities to spectra of parent hydrocarbons which are reasonably well understood. Sometimes, particularly in the high-frequency portion of the spectra, the resolution is so poor that no assignments were attempted. The positions of peaks and shoulders are rarely read off with an accuracy better than $\pm 25\text{ cm}^{-1}$.

ANALOGUES OF NAPHTHALENE

2-Methyl-2,1-borazonaphthalene (*I*). As pointed out by Dewar², the spectrum (Fig. 1) resembles that of isoquinoline. The first two transitions are cleanly separated; neither of them undergoes a temperature shift. The first band has origin at 31450 cm^{-1} and contains four progressions in 1350 cm^{-1} . The strongest of these is built on the 0–0 peak; the weaker ones originate at 0–0 + 500 cm^{-1} , 0–0 + 650 cm^{-1} , and

0-0 + 1150 cm^{-1} . The 0-0 peak is strongest and the purely electronic transition moment is undoubtedly much larger than in naphthalene. We did not attempt to determine it because at least some of the active vibrations could be acting similarly as the b_{3g} vibrations in naphthalene which are responsible for intensity borrowing from the second excited state⁶. However, in contrast to the first transition of naphthalene, vibronic intensity borrowing is not the predominant source of intensity. The 0-0 peak of emission is located 450 cm^{-1} below the 0-0 peak of absorption. In overall shape, the emission spectrum is a good mirror image of the first absorption band. This is confirmed by a more detailed inspection which shows a strong progression in 1300 cm^{-1} built on the 0-0 peak, and less distinct progressions in 1300 cm^{-1} built on 0-0 - 450 cm^{-1} and 0-0 - 650 cm^{-1} . The second absorption band originates at 37500 cm^{-1} . Two progressions in 1300 cm^{-1} are resolved, a strong one starting at the 0-0 peak and a weak one starting at 0-0 + 450 cm^{-1} . The change in the details of shape on going to room temperature suggests that other unresolved progressions are present. The transition is somewhat more strongly electronically allowed than the first one.

The indistinct shoulders at 41800 cm^{-1} and 43000 cm^{-1} (labelled a in Fig. 1) do not fit the vibrational spacings of the second band nor the shape of its Franck-Condon envelope and are assigned to the transition into the third excited state. Its origin probably lies

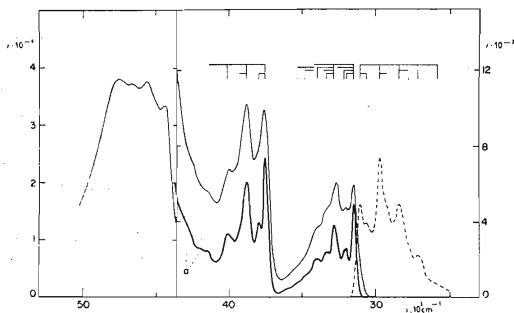


FIG. 1

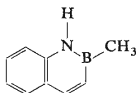
2-Methyl-2,1-borazaronaphthalene (I) (in 3-Methylpentane Solution)

Values of molar extinction coefficient ϵ refer to the room temperature absorption spectrum (thin line); vertical scales for the absorption spectrum at 77°K (thick line) and the emission spectrum (dashed) are arbitrary. Tentative vibrational analysis is indicated above the spectra (dotted lines indicate shoulders).

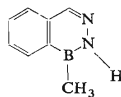
near 41 000–43 000 cm^{-1} , its intensity seems smaller than that of the first transition, its shape seems Franck–Condon forbidden, implying a somewhat different equilibrium nuclear geometry in the excited state. Little can be said about the higher frequency region. There are probably at least two strong transitions between 44 000 and 49 000 cm^{-1} . The 0–0 peak in phosphorescence spectrum is located at 23 600 cm^{-1} .

8a,4a-Borazaronaphthalene (II). The spectrum (Fig. 2) is superficially quite similar to that of naphthalene, or even more closely, quinoline, since it does not start with a very weak band (L_b in naphthalene). In a previous study⁷, the weaker part of the spectrum has been overlooked; the correspondence to naphthalene suggested there is wrong. According to the present results, the first band has an origin at 33 250 cm^{-1} ; the origin of fluorescence is only 150 cm^{-1} lower. At first glance, there is no similarity at all between the rather complex poorly resolved shape of the absorption band and the much simpler structure of the fluorescence spectrum, which consists of only two progressions in 1350 cm^{-1} , based on the 0–0 and 0–0 –650 cm^{-1} , respectively. Similar two progressions in 1350 cm^{-1} can be recognized in the absorption also; they originate at 0–0 and 0–0 +700 cm^{-1} . The resolution obtained is insufficient to rigorously exclude the possibility that the peaks assigned as members of two progressions all belong in reality to just one progression in 650–700 cm^{-1} , but the alternating intensities make it unlikely. The reason why absorption appears much more complicated is the additional presence of two strong progressions in 1350 cm^{-1} , apparently originating at 0–0 +1050 cm^{-1} and 0–0 +1750 cm^{-1} . For the same reason as above, we consider it unlikely that these peaks assigned as two progressions are in reality members of only one.

Some additional information can be obtained from low-temperature dichroic spectra (Fig. 3) in spite of their very poor resolution. It has been found⁸ for about 30 planar molecules, including naphthalene, that the kind and degree of orientation in stretched polyethylene is dictated by molecular shape. All orientate with the long axis along the stretching direction; it is highly likely that this is also the case for II. Inspection of the absorption curve recorded with plane-polarized light with electric vector parallel (E_{\parallel}) and perpendicular (E_{\perp}) to the direction of stretching shows that peaks 1–5 are long-axis and peaks 2'–5' short-axis polarized. "Reduced" absorption curves $E_{\parallel} - 0.7 E_{\perp}$ and $E_{\perp} - 0.7 E_{\parallel}$ corresponding to absorption polarized along the long axis and perpendicular to it were constructed as described elsewhere⁸ and are



II



III

included in Fig. 3. Unfortunately, noise and low resolution make them of little value beyond the first few peaks. Nevertheless, they suggest that 2' is not the first perpendicularly polarized absorption peak. A weaker peak, 1', appears to be present between 1 and 2' approximately 3–3.5 nm to the blue from peak 1. Two other choices of reduction factors are shown in Fig. 3 (dotted lines) to show that 1' cannot be removed by a different choice of these factors. It cannot be discerned in the unpolarized absorption spectrum in Fig. 2. Its position is indicated by a dotted line with a question mark, assuming that in 3-methylpentane it is also 3–3.5 nm to the blue from peak 1, as in polyethylene. It fits nicely into one of the "extra" progressions in 1350 cm^{-1} as its 0–0 band. If it is real, the origin of this progression lies at approximately $0-0 + 400\text{ cm}^{-1}$ instead of $0-0 + 1750\text{ cm}^{-1}$. Fig. 2 also shows polarizations of peaks 1–5 and 1'–5' as indicated by Fig. 3. The 0–0 component 1 of the first transition is polarized along the long axis. The 1350 cm^{-1} vibration which forms progressions is totally symmetrical; the 700 cm^{-1} and 650 cm^{-1} vibrations, one quantum of which provides the false origins of $0-0 + 700\text{ cm}^{-1}$ in absorption and $0-0 - 650\text{ cm}^{-1}$ in emission are of b_1 species and probably analogous to the 437.7 or 911.0 cm^{-1} b_{3g} vibrations in naphthalene⁶, where they are responsible for vibronic mixing with the second excited state. The presence of the two "extra" progressions could be explained as due to combinations with one quantum of a totally symmetrical 1050 cm^{-1} vibration and the possible presence of the peak 1' as due to one quantum of a b_1 400 cm^{-1} vibration. It would be somewhat unusual that no progression in the totally

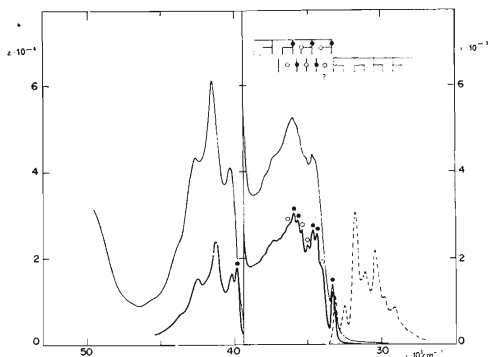


FIG. 2

8a, 4a-Borazaronaphthalene (II)

As in Fig. 1. Black and white dots indicate long-axis and short-axis experimental polarizations, respectively.

symmetrical 1050 cm^{-1} vibration is seen despite the intensity of the $0-0 + 1050\text{ cm}^{-1}$ peak.

Instead, we propose that the peak near 33650 cm^{-1} (" $0-0 + 400\text{ cm}^{-1}$ ") is an origin of a second electronic band, polarized perpendicularly to the long axis, and that the correct assignment of the " $0-0 + 1050\text{ cm}^{-1}$ " peak really is $0-0 + 700\text{ cm}^{-1}$ where $0-0$ now refers to the second electronic transition. The basis for this suggestion is first, the presence of two different electronic states in this region in the closely

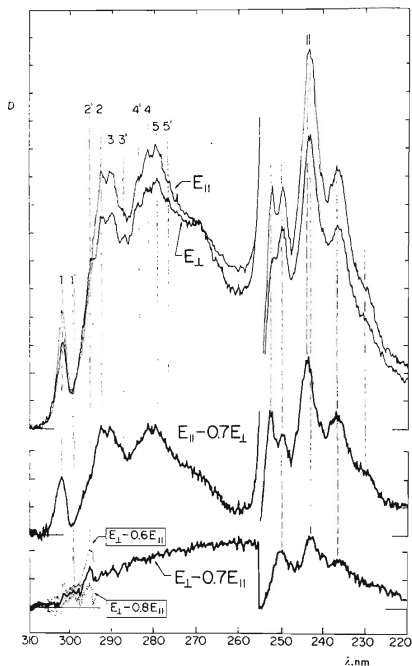


FIG. 3

8a, 4a-Borazaronaphthalene (II)

Computer-plotted dichroic spectra $E_{||}$ and E_{\perp} (corrected for baseline) and their linear combinations ("reduced spectra"). Stretched polyethylene sheet, 77°K . D optical density, arbitrary units.

related *I* and naphthalene, and second, the complete absence of peaks belonging to these two intense progressions in the fluorescence spectrum as contrasted with the good mirror-image symmetry in both *I* and naphthalene⁶. If this proposal is correct, the first two electronic bands are of similar intensity, comparable with that of the second transition in naphthalene. Neither undergoes a temperature shift and both are Franck–Condon forbidden. If our tentative identification of the 1' peak is incorrect, which is possible but unlikely, the second transition would be Franck–Condon allowed with 0–0 band at 34300 cm⁻¹, polarized along the long axis, and the perpendicular polarization of some of its components would be due to vibronic interaction with a higher-lying state.

At room temperature the 40000–45000 cm⁻¹ region of the spectrum seems to contain a single strong transition with origin at 40300 cm⁻¹ and a progression in a 1200 cm⁻¹ vibration. At 77°K little narrowing is observed, and the apparent origin splits into two, at 39800 and 40150 cm⁻¹. A tentative explanation is that two overlapping electronic bands of comparable intensity are present and one is red-shifted more than the other when the temperature is lowered. Fig. 3 shows that the peak at 39800 cm⁻¹ is polarized along the long axis. We assign it as the 0–0 band of the third electronic transition. Fig. 3 also shows that the apparently single band between 40000–45000 is a very complicated superposition of peaks of both polarizations. It seems that this must be due to the presence of two mutually perpendicularly polarized transitions in this region, since it is highly unlikely that the rather intense perpendicularly polarized components would arise from vibronic mixing of the strong

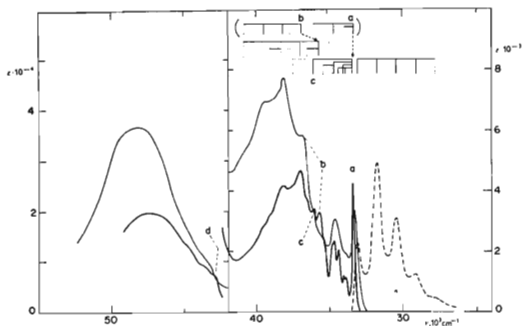


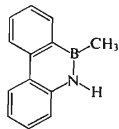
FIG. 4

4-Methyl-4,3-borazaroisoquinoline (III)

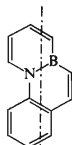
As in Fig. 1. Tentative vibrational analysis of the room-temperature spectrum shown in parentheses.

third (long-axis polarized) transition with the weak presumably perpendicularly polarized second transition, and the spectrum contains no other perpendicular transitions up to at least about 50000 cm^{-1} , where the next strong band is located. The 0–0 peak of phosphorescence lies at 22700 cm^{-1} . This molecule clearly deserves a vapor-phase high-resolution study.

4-Methyl-4,3-borazaroisoquinoline (III). As pointed out by Dewar², the spectrum (Fig. 4) resembles that of quinazoline. From band shapes and intensities in the spectrum at 298°K , the low-intensity region contains two bands with origins (a and b in Fig. 4) at 33300 and 36800 cm^{-1} , respectively, the second being considerably stronger. Both have one predominant progression in a 1350 cm^{-1} vibration. On going to 77°K the distinction between the two bands becomes less clear. The peaks belonging to the first Franck–Condon-allowed band can still be discerned owing to the fact that they undergo no temperature shift. The strong 0–0 peak (a in Fig. 4) is located at 33350 cm^{-1} . It is followed by components at 0–0 + 500, 0–0 + 650, 0–0 + 1000 ($= 2 \times 500$?), 0–0 + 1300 ($= 2 \times 650$?) and 1400 cm^{-1} ; then the sharpness is largely lost. The two room-temperature shoulders at 35450 and 36000 cm^{-1} can be identified as a shoulder and a peak at the same locations in the 77°K spectrum. Relative to the 298°K spectrum, the intensity of the latter (c in Fig. 4) is enhanced. There is an additional distinct peak at 35680 cm^{-1} (b in Fig. 4) without analogy at 298°K . The emission 0–0 peak is 350 cm^{-1} below the 0–0 peak of absorption. Only one progression of broad peaks is seen (1350 cm^{-1}). The emission is a fair mirror image of the first band in the room-temperature absorption spectrum; it lacks the better resolution of the absorption spectrum at 77°K . All peaks of the stronger, Franck–Condon forbidden band of the 298°K spectrum show a large red shift on going to 77°K (1250 cm^{-1}). The shape of the part above 38000 cm^{-1} is preserved. When an attempt is made to locate the shoulder which started the band in the 298°K spectrum, assuming it undergoes the same temperature shift, it is identified as the “extra” peak at 35680 cm^{-1} in the 77°K spectrum b, now in the region of the first band. This is assigned as the 0–0 peak of the second band. This band overlap also provides a natural explanation of the surprisingly high intensity of the peak c at 36000 cm^{-1} which belongs to the first band. A third, not much stronger band is seen as



IV



V

several shoulders starting at 42800 cm^{-1} in the 77°K spectrum (labelled d). Additional transitions must be responsible for the broad maximum at 47500 cm^{-1} but assignments are not possible. The $0-0$ peak of phosphorescence is observed at 23000 cm^{-1} .

ANALOGUES OF PHENANTHRENE

10-Methyl-10,9-borazarophenanthrene (IV). The spectrum (Fig. 5) bears some resemblance to those of phenanthrene derivatives; similarity to phenanthridine has been pointed out before². However, band positions correspond more closely to those of phenanthrene and many are at even higher energies, so that the trough near $43000-45000\text{ cm}^{-1}$, typical of phenanthrene and many of its derivatives, is completely missing. Like in phenanthrene itself⁹, the fluorescence spectrum is a good mirror image of the lowest absorption band. Both are Franck-Condon allowed and their $0-0$ peaks differ by 200 cm^{-1} . The emission shows a strong progression in 1300 cm^{-1} based at the $0-0$ peak and one presumed member of a 1300 cm^{-1} progression based on $0-0 - 700\text{ cm}^{-1}$, which is very poorly resolved. Other weaker components are believed to be present but unresolved. In absorption, a progression in 1300 cm^{-1} starting at the $0-0$ peak at 30650 cm^{-1} is by far the strongest. The first two members of a weak progression in 1300 cm^{-1} starting at $0-0 + 650\text{ cm}^{-1}$ are resolved. Two additional shoulders are seen at 33650 cm^{-1} and 35000 cm^{-1} (labelled a in Fig. 5). We tend to assign them as members of a 1300 cm^{-1} progression based at $0-0 + 400\text{ cm}^{-1}$, or perhaps $0-0 + 1700 (= 650 + 1050\text{ cm}^{-1})$ rather than as belonging to a different electronic transition since the temperature shift in the whole 30000 to 35000 cm^{-1} region is uniform (250 cm^{-1}) and because of the striking similarity

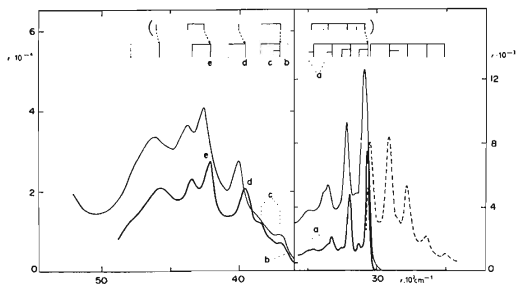


FIG. 5

10-Methyl-10,9-borazarophenanthrene (IV)

As in Fig. 1. Tentative vibrational analysis of the room-temperature spectrum shown in parentheses.

of the fine structure to that of the first band of phenanthrene (the two shoulders correspond to the e_0 and e_1 peaks in ref.¹⁰). The main difference between the two is that a considerable part of the intensity of the first band in phenanthrene is borrowed from the second band through a 700 cm^{-1} b_1 vibration while almost all of the much larger intensity of the first band of IV is purely electronic and the progression based on the probably analogous 650 cm^{-1} vibration is very weak. Comparison of temperature shifts suggests a grouping of peaks at higher frequencies into four electronic transitions as indicated in Fig. 4. The lowest of these c has a Franck-Condon forbidden shape. It is preceded by a very indistinct shoulder at 36500 cm^{-1} with an unclear assignment b. The 0-0 peak of phosphorescence is located at 23800 cm^{-1} .

10a,4a-Borazarophenanthrene (V). This spectrum (Fig. 6) looks much more like the spectrum of phenanthrene, particularly in the high-energy region. However, the phenanthrene L_b and L_a bands are now apparently replaced by one poorly resolved band of medium intensity. Origins of absorption and emission coincide within 100 cm^{-1} . The fluorescence spectrum shows a progression in approximately 1400 cm^{-1} , starting at 0-0, a less distinct one starting at 0-0 -400 cm^{-1} , and some indications of a third one starting at 0-0 -1000 cm^{-1} . Except for the 0-0 and 0-0 -400 cm^{-1} peaks the resolution seems poorer than usual and the spacing is somewhat irregular. This indicates that several unresolved vibrations of wavenumbers close to 1400 cm^{-1} are active. In absorption, the first three peaks (a, b in Fig. 6) are sharp but then the situation is even worse. The overall appearance can be explained by assuming 1400 cm^{-1} progressions based on the 0-0 peak, on 0-0 $+300\text{ cm}^{-1}$, 0-0 $+450\text{ cm}^{-1}$, and 0-0 $+1000\text{ cm}^{-1}$ as indicated in Fig. 6. However, it is perhaps

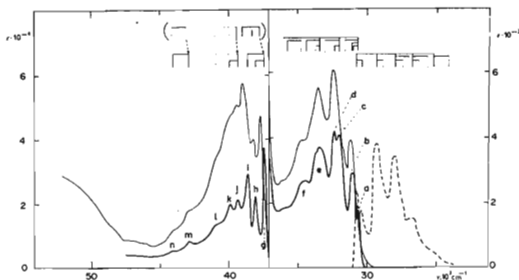


FIG. 6

10a,4a-Borazarophenanthrene (V)

As in Fig. 1. Tentative vibrational analysis of the room-temperature spectrum shown in parentheses.

more likely that the unusual blurring is due to the presence of two transitions in this region. There are three indications that this might be the case. First, the spectrum at 77°K has just as broad bands as the 298°K spectrum; this could happen if the two transitions happen to overlap more exactly at 298°K and have slightly different temperature shifts. Second, in spite of the lower resolution due to the instruments used, emission bands are narrower in this case than those of absorption. Finally, overall similarity to phenanthrene suggests that the medium-intensity absorption regions should contain two separate transitions. The group of peaks at 37000 to 41000 cm^{-1} (g-l) is due to at least two independent transitions judging by the fact that the temperature shift of the first three peaks (g, h, i) is 300–400 cm^{-1} , while the others are barely affected at all. The region of very strong absorption of phenanthrene near 40000 cm^{-1} also contains two separate transitions^{8,11}. The shoulder l at 40900 cm^{-1} might belong to another independent transition rather than be related to the peaks at 39300 and 39900 cm^{-1} by the somewhat unusually large interval 1600 cm^{-1} as indicated in Fig. 6. The two peaks at 42800 and 43100 cm^{-1} (m, n) undoubtedly belong to a separate transition. Some information on the direction of polarization of the individual peaks in the spectrum of *V* has been obtained recently from low-temperature measurements of dichroism in stretched polyethylene sheet and comparison with results for phenanthrene¹². The deviation $|\varphi|$ of the transition moment directions from the effective orientation axis, assumed to coincide with the axis indicated in formula *V*, decreases in the order $|\varphi_a| > |\varphi_j| = |\varphi_l| > |\varphi_m| = |\varphi_n| > |\varphi_h| > |\varphi_c| = |\varphi_d| > |\varphi_e| = |\varphi_f| > |\varphi_k| = |\varphi_g| = |\varphi_i|$. The results for

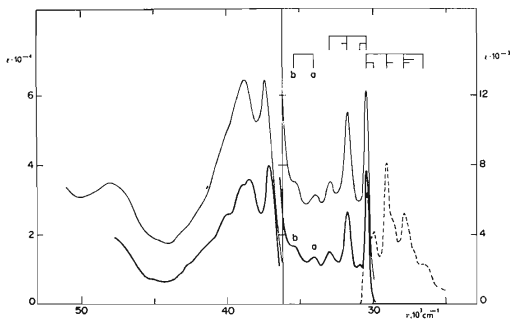


FIG. 7

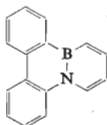
12b,4a-Borazarotriphenylene (VI)

As in Fig. 1.

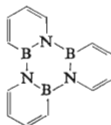
peaks c, d, e, f are somewhat less reliable because of poor resolution. However, it seems that most if not all of the strong overlapping peaks in that region have similar values of $|\varphi|$. With virtually no assumptions about the orientation distribution of V in stretched polyethylene, the following values have been derived¹² for $|\varphi|$ (in parentheses, range of values obtained assuming that V orientates somewhat similarly as phenanthrene, if narrower than the above): $|\varphi_a| = 54-90^\circ$ (54-73); $|\varphi_c| = |\varphi_d| = 30-51^\circ$; $|\varphi_e| = |\varphi_f| = 21-48^\circ$ (28-48); $|\varphi_g| = 0-40^\circ$ (19-40); $|\varphi_h| = 35-53^\circ$; $|\varphi_i| = 0-40^\circ$ (19-40); $|\varphi_j| = 46-83^\circ$ (46-68); $|\varphi_k| = 0-41^\circ$ (16-41); $|\varphi_l| = 40-90^\circ$ (40-74); $|\varphi_m| = |\varphi_n| = 40-66^\circ$. The results are compatible with our tentative decomposition of the spectrum into individual electronic transitions as indicated in Fig. 6.

ANALOGUES OF TRIPHENYLENE

12b,4a-Borazarotriphenylene (VI). The spectrum of VI (Fig. 7) resembles the spectrum of 1,4-diazatriphenylene¹¹ much more than that of triphenylene¹³⁻¹⁵ itself; this is understandable from symmetry considerations. The 0-0 peak of the first absorption band at 30400 cm^{-1} coincides with that of fluorescence. Progressions in 1300 cm^{-1} are seen in both; in emission, based on the 0-0, 0-0 - 500 cm^{-1} and 0-0 - 750 cm^{-1} (only one member resolved), in absorption, based on the 0-0 and 0-0 + 400 cm^{-1} peaks. The mirror image symmetry is rather good. The peaks at 34000 and 35400 cm^{-1} (a and b in Fig. 7) do not fit the regular progression nor the Franck-Condon envelope and are assigned as a second transition, of slightly lower intensity. None of the peaks under 36000 cm^{-1} undergoes a temperature shift. The more intense group of peaks above 36000 cm^{-1} is red shifted by about 300 cm^{-1} when the temperature is lowered. It probably contains more than one transition but poor resolution prevents more definite assignments. The same holds for the absorption maximum at 48000 cm^{-1} .



VI



VII

4b,8b,12b,4a,8a,12a-Triboratriazarotriphenylene (VII). As pointed out by Dewar², the spectrum (Fig. 8) is quite similar to that of triphenylene¹³⁻¹⁵. In both cases, the 0-0 absorption and emission peaks are very weak in contrast to compounds I-VI. This suggests that the transition is symmetry forbidden. By analogy¹³ to triphenylene and benzene, one could expect the first strong peak to be due to

a simultaneous excitation of an e' vibration, acting as a false origin for a progression in a totally symmetrical vibration. The frequency of this e' vibration has been assigned as 525 cm^{-1} in triphenylene¹³ (404 cm^{-1} in benzene). It seems that in the fluorescence spectrum of *VII* the e' vibration is 650 cm^{-1} . Starting at $0-0 - 650\text{ cm}^{-1}$, all peaks of the emission can be fitted into regular pattern involving presumably totally symmetrical vibrations with wavenumbers 700 , 1150 , and 1300 cm^{-1} . The repeated interval is 1300 cm^{-1} (in triphenylene: 1375). In contrast to triphenylene, only combinations involving also a quantum of the 700 cm^{-1} vibration are intense (and less so, combinations involving also a quantum of the 1150 cm^{-1} vibration). However, other interpretations of the emission spectrum are possible and equally likely, assuming more than one e' vibration is active in making the transition allowed. One such possibility is also shown in Fig. 8. The absorption spectrum undergoes no temperature shift. It starts by two very poorly resolved shoulders (a in Fig. 8), the first of which, at 30600 cm^{-1} , coincides with the origin of fluorescence and is presumably the $0-0$ peak. A similar double peak appears in the published low-temperature absorption spectra of triphenylene^{14,15}. In the absorption of *VII*, the double shoulder is followed by several rather closely spaced peaks. There is very little superficial similarity to emission. Tentatively, one could assign the interval between the two shoulders to an e' vibration (460 cm^{-1}), analogous to the 650 cm^{-1} vibration in emission, accounting for the fact that the second shoulder is much stronger. The following peaks are then presumably due to various totally symmetrical vibrations and/or their combinations. Again, it is possible that more than one e' vibration is active. No more definite conclusions are possible from the data available. A second symmetry-

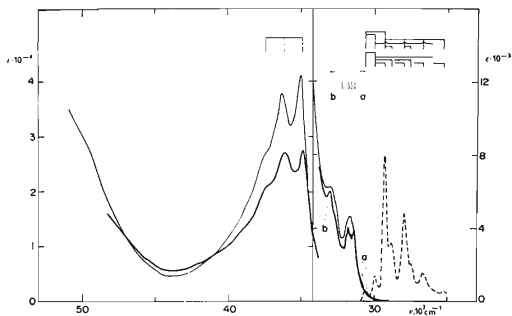


FIG. 8

4a,8b,12b,4a,8a,12b-Triboratriazarotriphenylene (*VII*)

As in Fig. 1. Two of the possible vibrational analyses of the emission spectrum are indicated.

forbidden transition (b in Fig. 8) seems to have origin at 32700 cm^{-1} and the first peak is again due to one quantum of the 400 cm^{-1} e' vibration. This would be analogous to the situation in triphenylene¹³. The region of weak absorption is followed by a strong band showing 3 or more components of a progression in 1250 cm^{-1} . This is again similar to triphenylene, where the vibration involved is 1325 cm^{-1} . The transition is allowed, the symmetry of the excited state undoubtedly is E' . The next strong band comes only above 50000 cm^{-1} .

DISCUSSION

To obtain safe knowledge of the number of independent electronic transitions present and their assignments it would seem necessary to investigate the effects of substitution. This in turn requires an extensive synthetic and spectroscopic effort. Our present results only represent a first step in this direction. In our analysis of the spectra, we have tried to point out the weak points; it is much more likely that some transitions have been overlooked than that too many have been found.

According to our results, in the region below about 40000 cm^{-1} the number and energies of excited states of molecules *I–VII* generally resemble quite closely those of the parent hydrocarbons. Above 40000 cm^{-1} , the differences seem larger, more separate electronic bands apparently being seen in the spectra of the borazaro compounds. The largest difference between the two sets of spectra is the absence of very weak first bands¹⁶ in the spectra of *I–VI*. This provides the spectral curves of *I–VI* with more similarity to spectra of aza analogues of the parent benzenoid hydrocarbons than to the spectra of the hydrocarbons themselves². The only exception is *VII*. In this case, however, the forbidden nature of the first two transitions is undoubtedly due to symmetry factors.

It seems likely that the electronic structure of the borazaro compounds is quite similar to that of the parent alternant hydrocarbons, and even more, their aza analogues, as claimed by Dewar^{1,2}. In terms of current π -electron models, the "almost forbidden" nature of some of the symmetry-allowed transitions in alternant hydrocarbons is due to orbital-pairing properties^{2,17,18} which are no longer present in aza analogues. Both the absence of a weak first band and the probable presence of additional transitions at higher energies, presumably corresponding to unobserved weak hydrocarbon bands buried under strong absorption, can be explained by assuming that orbital-pairing is also absent in the borazaro compounds.

A more detailed discussion of the spectral results requires a comparison with calculations and is presented in a following paper⁴.

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