

**BORAZARO ANALOGUES
OF AROMATIC HYDROCARBONS. II.*
SEMIEMPIRICAL CALCULATIONS**

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

Received June 4th, 1970

Semiempirical π -electron Pariser-Parr-Pople calculations on borazaro analogues of aromatic hydrocarbons give good results for electronic spectra, ionization potentials, and ^{11}B NMR chemical shifts. A reinterpretation of existing experimental data is proposed in some instances. Numerous predictions are made for presently unknown compounds.

While numerous calculations¹ have been reported by various authors for borazine, fewer have been published for other borazaro heterocycles, and none of the latter concentrated on spectral properties. In the present paper, values of parameters for boron and nitrogen needed in the Pariser-Parr-Pople (PPP) method are derived by empirical adjustment to a small fraction of the spectral information reported in a preceding paper². PPP calculations are then used to interpret the electronic spectra of molecules *I–VII*; the results also account well for the known ionization potentials and ^{11}B NMR chemical shifts. Finally, predictions for two dozen presently unknown borazaro heterocycles are made.

To facilitate reference to the experimental paper², the numbers assigned there to molecules *I–VII* are retained in the present paper. The formulas are shown in Chart I.

CALCULATIONS

Method. We have used the π -electron approximation, in spite of its obvious shortcomings, because of first, the size of molecules *I–VII*, and second, the presently still rather unsatisfactory stage of development of more sophisticated semiempirical methods for spectral calculations. Because of this rather drastic approximation we felt it would be appropriate to use a very simple version of the semiempirical self-consistent-field PPP method³: all bonds were assumed to be of equal length (1.40 Å, regular hexagons), two-center electron repulsion integrals were calculated according to Mataga and Nishimoto⁴, penetration and non-neighbor resonance integrals were neglected. Configuration interaction was limited to singly excited configurations with excitation energies 8 eV or less (10 eV or less for benzene analogues). This simple approach gives good

* Part I: This Journal 36, 1233 (1971).

results for hydrocarbons without strong bond-length alterations, and their heterocyclic and substituted derivatives (for references see refs^{5,6}).

Of the several proposed models, we have chosen the one according to which boron contributes no electrons ($Z = 0$) and nitrogen two electrons ($Z = 2$) to the π -system as physically most appealing. Redistribution of π -electrons into molecular orbitals then automatically provides B^-N^+ polarity in the π -system while the B^+N^- polarity of the σ -skeleton steps in indirectly through its effect on atomic parameters for boron and nitrogen.

The matrix elements of the SCF Hamiltonian are well known to be³

$$F_{ii} = -I_i + \frac{1}{2}q_i\gamma_i + \sum_{j \neq i} (q_j - Z_j) \gamma_{ij}$$

$$F_{ij} = \beta_{ij} - \frac{1}{2}p_{ij}\gamma_{ij},$$

where q stands for π -electron density, p for bond order, γ for electron-repulsion integrals, β for resonance integrals, I for the valence state ionization potential. Further, $\gamma_i = I_i - A_i$, where A is the valence state electron affinity.

Parameters. Because of the very approximate nature of the calculations, we can only expect to obtain meaningful results in those instances where they are not critically dependent on the choice of parameters. We are not aware of any previous detailed effort to find which values, or ranges of values, of parameters for boron and nitrogen in borazaro aromatic compounds are best suited for use in the PPP model (many such studies have been published for amino and imino nitrogen; see *e.g.* ref.⁶ for leading references). The latter values should be a reasonable approximation for nitrogen in the borazaro heterocycles, but need not be optimum because of the inductive effect of adjacent boron and the much higher positive charge on nitrogen than is usual in amines. By far most of the previous workers desired to obtain results for borazine itself and had to derive parameter values from *a priori* estimates and guesses, since the only available data to which the parameters could have been adjusted were those for borazine itself. Such *a priori* estimates from atomic properties are unlikely to provide more than a wide range of probable values, particularly for atoms which donate two or no electrons to the π -system and acquire relatively high charges. Factors contributing to the uncertainties are lack of detailed information about the σ -skeleton (core charges), about bond lengths, and the circumstance that the parameters are supposed to somehow compensate for the many neglects made in the crude method of calculation.

Since we now have at hand an abundance of quantitative experimental data², we can afford to use a small fraction of it for parameter adjustment, using as guidance the ranges of values obtained by others from *a priori* estimates, and then interpret the rest of our data by means of calculations using these parameters. Attempts to use correlations of polarographic half-wave potentials⁷ and of ¹¹B NMR chemical shifts⁸ with orbital energies and π -electron densities on boron, respectively, were not successful. No correlation was found for the former, while good correlation irrespective of parameter choice was found for the latter.

To keep the number of adjustable parameters manageable, we make no difference between bridgehead boron atoms, bonded to nitrogen and two aromatic carbons, and other boron atoms bonded to a methyl group, an aromatic carbon and nitrogen. In molecules with more than one BN pair, no allowance is made for the number of heteroatoms bonded to a given boron or nitrogen. Moreover, σ -inductive effects of heteroatoms on adjacent carbons are disregarded. All carbon parameters were taken over from previous work of the Prague group⁹. This still leaves a formidable array of adjustable parameters: β_{CB} , β_{CN} , β_{BN} , I_{B^-} , A_{B^-} , I_{N^+} , A_{N^+} .

The range of values for parameters which was investigated as physically reasonable was for β 's, -2.318 eV ($= \beta_{CC}$) to -1.7 eV; for I_{B^-} , from -1 to $+4$ eV; for A_{N^+} , from 6 to 9.5 eV;

TABLE I
 Analogues of Naphthalene (VIII)^a

Position ^b		Excited singlets ^c							$I P^d$	q_B^e	q_N^f	$P_{BN}(P_{CC})^g$
B	N	1	2	3	4	5	6	7				
None	ΔE	33.4	35.3	45.7	45.9	46.1	49.0	50.7	(8.11), 9.09			
	f	0	0.25	2.04	0	0	0	0.58	10.12, 11.07			
	φ	—	90	0	—	—	—	90	12.88			
2	ΔE	(32.4)	(37.1)	43.5	45.5	49.0	49.4	8.41, 8.66	10.50, 10.92	0.425	1.528	0.587 (0.742)
	f	(0.15)	(0.19)	0.70	0.76	0.38	0.39	10.50, 10.92	13.15			
	φ	135	30	162	25	109	40	13.15				
8a	ΔE	33.2	33.4	41.4	43.9	47.1	51.5	(8.27), 8.63	10.29, 11.19	0.558	1.359	0.476 (0.543)
	f	0.06	0.05	0.93	0.85	0.04	0.93	10.29, 11.19	13.25			
	φ	90	0	0	90	0	0	13.25				
4	ΔE	34.0	36.8	44.0	47.3	48.6	49.5	8.13, 9.37	9.83, 11.82	0.414	1.489	0.613 (0.742)
	f	0.15	0.25	0.60	0.19	0.81	0.33	9.83, 11.82	13.16			
	φ	4	135	17	91	179	128	13.16				
1	ΔE	32.9	36.0	43.8	47.0	48.2	49.9	7.79, 9.19	9.75, 11.43	0.412	1.516	0.583 (0.742)
	f	0.14	0.34	0.49	0.47	0.23	0.42	9.75, 11.43	12.67			
	φ	149	31	153	18	171	16	12.67				
2	ΔE	28.6	34.6	40.3	42.4	45.1	49.2	7.57, 9.27	9.92, 11.42	0.498	1.423	0.525 (0.586)
	f	0.35	0.008	0.17	0.04	1.71	0.09	9.92, 11.42	12.98			
	φ	95	97	7	142	3	117	12.98				
1	ΔE	27.3	29.9	42.8	43.8	47.9	50.9	7.57, 9.55	10.70, 11.17	0.484	1.366	0.475 (0.539)
	f	0.13	0.36	0.77	0.10	0.14	0.51	10.70, 11.17	13.72			
	φ	116	9	29	159	148	135	13.72				
8a	ΔE	28.9	30.2	43.5	44.3	47.3	51.1	7.92, 8.41	10.10, 11.12	0.554	1.422	0.484 (0.539)
	f	0.28	0.20	0.87	0.03	0.45	0.32	10.10, 11.12	12.64			
	φ	155	36	41	127	154	148	12.64				

TABLE I
(Continued)

Positions		Excited singlets							I^P	q_B	q_N	$P_{BN}(P_{CC})$
B	N	1	2	3	4	5	6	7				
5, 8a	4a, 8	ΔE 33.5 f 0.003 φ 101	34.8 0.27 91	40.9 0.64 16	44.1 0.41 93	47.8 0.15 88	50.5 0.85 166	8.06, 10.16, 12.76	8.77 (8a) 0.557 (5) 0.405	(4a) 1.393 (8) 1.530	(8a, 8) 0.457 (0.539) (4a, 8a) 0.492 (0.543) (4a, 5) 0.448 (0.539)	
1, 3	2, 4	ΔE 33.3 f 0.10 φ 92	38.5 0.04 8	45.4 1.38 175	46.9 0.31 73	49.4 0.08 123	8.13, 9.99, 12.85	9.06 10.87 12.85	(1) 0.371 (3) 0.435	(2) 1.553 (7) 1.589	(1, 2) 0.579 (0.742) (2, 3) 0.548 (0.586) (3, 4) 0.568 (0.742)	
4, 5, 8a	1, 4a, 8	ΔE 36.1 f 0.42 φ 90	37.8 0.03 0	43.7 0.34 0	46.1 0.20 0	47.2 0.25 90	49.1 0.43 0	8.10, 9.91, 12.71	8.89 (8a) 0.551 (8) 0.403	(4a) 1.440 (1) 1.576	(1, 8a) 0.480 (0.539) (4a, 8a) 0.508 (0.543) (4, 4a) 0.481 (0.539)	
5, 7, 8a	4a, 6, 8	ΔE 32.8 f 0.22 φ 84	39.5 0.06 122	45.1 0.72 13	47.7 0.12 38	48.2 0.23 137	50.1 0.58 166	8.04, 10.05, 12.62	9.19 10.73 (8a) 0.527	(8) 1.587 (6) 1.567 (4a) 1.432	(4a, 8a) 0.475 (0.543) (4a, 5) 0.445 (0.539) (5, 6) 0.605 (0.742) (6, 7) 0.510 (0.586) (7, 8) 0.598 (0.742) (8, 8a) 0.466 (0.539)	
2, 4, 5, 7, 8a	1, 3, 4a, 6, 8	ΔE 42.1 f 0.0007 φ 0	43.3 0.13 90	48.3 1.11 0	51.6 0.16 90	8.60, 9.78, 11.88	9.11 10.45 (8a) 0.501	(2) 0.415 (4) 0.387 (8a) 0.501	(3) 1.583 (4a) 1.507 (1) 1.611	(1, 2) 0.565 (0.742) (2, 3) 0.536 (0.586) (3, 4) 0.568 (0.742) (4, 4a) 0.483 (0.539) (4a, 8a) 0.458 (0.543) (1, 8a) 0.488 (0.539)		

^a Values in parentheses were used for parameter adjustment. ^b See Chart I. ^c ΔE Excitation energy in 10^{-3} cm^{-1} units; f oscillator strength; φ angle between the transition moment direction and the x-axis in Chart I (counterclockwise, in degrees). ^d Ionization potentials for π -electrons (see footnote in Table IX). ^e π -Electron density at boron. ^f π -Electron density at nitrogen. ^g p : B—N bond order; P_{CC} : bond order in the corresponding position of the parent hydrocarbon.

for γ_B , from 6 to 9.84 eV ($= \gamma_C - 1$ eV); for γ_N , from 11.84 eV ($= \gamma_C + 1$ eV) to 17 eV. The range of the β 's was guessed from values obtained from the gradient of overlap formula¹⁰ using Slater orbitals with effective charges corresponding to B, B⁻, C, N⁺, N, and bond lengths estimated from those of related compounds. The ranges for I and A were estimated *a*) on basis of changes in the nature of the "best" $2p$ orbital expected on going from C to the less electronegative B or more electronegative N, using the fact that $I_{B^-} = 6$ eV or $A_{N^+} = 6$ eV would correspond to the heteroatom having electronegativity effectively equal to that of carbon [$(I_C + A_C)/2 = 6$ eV; for a more detailed discussion see ref. ⁶], *b*) by comparison with values used by others for B and N, *c*) by comparison with the values I_{B^-} (1–2 eV) and A_{N^+} (7.5 eV) which give best accounts of the spectra of 9-ethyl-9-boraffluorene and carbazole, using the same parameters for carbon⁶ (these results are insensitive to γ_N and γ_B).

About a dozen calculations for molecules *I–VII* and several dozen more for each of *I*, *II*, and *IV* showed that the basic features of calculated spectra (number of transitions and their approximate energies) fortunately depend very little on the parameter values chosen within the above limits. This allowed a tentative assignment of calculated to observed transitions. The "best" values were then found arbitrarily as those which best reproduced *a*) the difference of the reported gas-phase first ionization potentials¹¹ (IP) of naphthalene (8.11 eV) and *II* (8.24 eV), *b*) the excitation energies and relative intensities of the first two transitions in *I*, and *c*) the excitation energy of the first transition in *VII*. To fit *a*), the values of γ_N and γ_B have to be close to the value for carbon ($\gamma_C = 10.84$ eV). Condition *b*) mostly restricts the possible values of I_{B^-} and A_{N^+} and requires that $\beta_{CN} \cong \beta_{CC}$, while condition *c*) has mostly the effect of not permitting too low values for β_{BN} and β_{CB} .

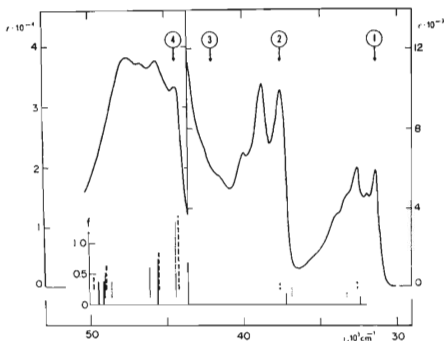


FIG. 1

Room-Temperature Absorption Spectrum of 2-Methyl-2,1-borazaronaphthalene (*I*) in 3-Methylpentane with Approximate Positions of Origins of Individual Electronic Transitions, taken from ref. 2

Below, calculated energies and intensities of transitions using parameter sets A (full lines), B (dotted lines) and C (dashed lines). The scale for oscillator strength f applies to set A; results for sets B and C are displaced upwards by 0.125 and 0.25 units of f , respectively.

Several almost equally good parameter sets were found near the "optimum" values. To show the insensitivity of calculated spectra to minor details of parameterization, results for three parameter sets are shown in the lower parts of Figs 1–7: the "best" set A (full line, $\beta_{BC} = \beta_{CN} = -2.318$ eV, $\beta_{BN} = -2.0$ eV, $I_{B^-} = 1.5$ eV, $\gamma_B = 9.84$ eV, $A_{N^+} = 8.8$ eV, $\gamma_{N^+} = 11.84$ eV), and the sets B (dotted line, $\beta_{CB} = \beta_{CN} = \beta_{BN} = -2.318$ eV, $I_{B^-} = 2.5$ eV, $\gamma_B = 9.84$ eV, $A_{N^+} = 8$ eV, $\gamma_N = 11.84$ eV) and C (dashed line, $\beta_{CB} = \beta_{CN} = \beta_{BN} = -2.318$ eV, $I_{B^-} = 1.0$ eV, $\gamma_B = 9.84$ eV, $A_{N^+} = 8$ eV, $\gamma_N = 11.84$ eV). The differences between the calculated *IP* of *II* and the calculated *IP* of naphthalene are 0.16, 0.16 and 0.19 eV for A, B, and C, respectively; the experimental value is 0.13 eV.

For *III*, parameter values for aza nitrogen are also required. We have repeated the calculations using three sets of nitrogen parameters: those recommended by Koutecký¹² ($I_{N(\text{aza})} = 16.55$ eV, $\gamma_{N(\text{aza})} = 14.77$ eV, $\beta_{CN(\text{aza})} = -2.7$ eV), with a) $\beta_{NN} = \beta_{CC}$ and b) $\beta_{NN} = -1.8$ eV, and the "less electronegative" values $I_{N(\text{aza})} = 13.92$ eV, $\gamma_{N(\text{aza})} = 11.84$ eV, $\beta_{CN} = -2.70$ eV, with $\beta_{NN} = \beta_{CC}$, close to those recommended by Tichý and Zahradník¹³ and more compatible with our value for γ_N . All three choices give very similar results. Results shown in Fig. 3 and in Table I were obtained with the last named set.

Selected results of the calculations using parameter set A are summarized in Tables I–VIII, using notation of Chart I. Charge distributions, bond orders, π -electron components of dipole moment in ground and excited states and other results for these and additional related molecules are available from the author on request. It should be remembered that in all formulas presence of a methyl group on boron is assumed unless it is in a bridgehead position.

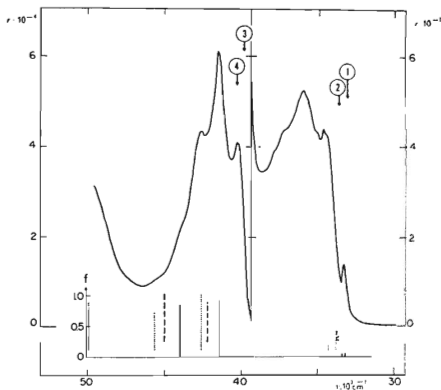


FIG. 2

8a,4a-Borazaronaphthalene (*II*)

As in Fig. 1.

RESULTS AND DISCUSSION

ELECTRONIC SPECTRA

Results of calculations are shown in Figs 1–7 along with absorption curves and positions of 0–0 bands of the individual electronic transitions wherever these have been established with reasonable certainty. All experimental data are from ref.². In comparing calculated and experimental transition energies it should be remembered that the former correspond to vertical transitions. In case of bands with Franck-Condon forbidden shape the vertical excitation energy will be somewhat higher than the 0–0 band energy, and it is often not clear how much.

Analogues of naphthalene (Table I, Figs 1–3). Naphthalene spectrum in the near UV region¹⁴ consists of a weak band starting at $31\,300\text{ cm}^{-1}$ (L_b in Platt's notation¹⁵), a medium-intensity band starting at $35\,000\text{ cm}^{-1}$ (L_a), and a strong band at $45\,200\text{ cm}^{-1}$ (B_b). The L_a band is polarized along the short axis, B_b along the long axis. The electronically allowed part of the L_b band is very weak ($f = 0.0002\text{--}4$ in the gas phase¹⁶) and is polarized along the long axis; about ten times more intensity is "borrowed" from the L_a band through 437.7 cm^{-1} and 911 cm^{-1} b_{3g} vibrations. Simple PPP calculations are in good agreement with these observations ($f = 0$ is predicted for the

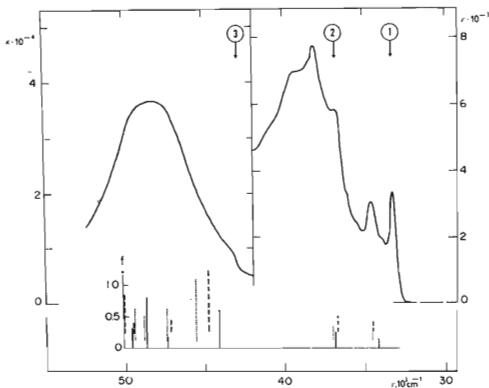


FIG. 3.

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

As in Fig. 1.

L_a band). However, they also predict the presence of additional forbidden transitions (Table I). These should occur in the region of strong absorption due to allowed bands and must be rather hard to detect. The parameters related to the effective electronegativities of boron and nitrogen in our calculations have been chosen so as to reproduce the fact that the first two bands in *I* have comparable intensities. The same values also correctly predict that the same should hold for *II* and *III*. Moreover, they reproduce correctly the fact that the sum of the intensity of the first two bands is noticeably higher in *I* and *III* than in *II*. The most striking difference between the spectra of *I*, *II*, and *III* (Figs 1–3) is the varying separation of the first two bands: the origins differ by 6050 cm^{-1} in *I*, 2330 cm^{-1} in *III* (maxima by 3550 cm^{-1}) and 400 cm^{-1} (or possibly 1050 cm^{-1}) in *II*. This and even the absolute band locations in all three are again in good agreement with calculations. The agreement of the positions of the first two bands in *I* with calculations is a result of parameter adjustment. However, the correct result that the gap between them is larger than in *II* and *III* is insensitive to the choice of parameters. It appears that it is not necessary to take into account changes in resonance integrals due to variation in bond lengths, as suggested by Dewar¹⁷, in order to explain the varying degree of separation of the first two excited singlet states.

Experimental results make it likely that the first two bands in *II* are polarized perpendicular to each other. This is also the result obtained from calculations quite independently of parameter choice. The order of predicted absolute polarizations is very sensitive to parameters since the transitions are almost degenerate. If the order of vertical transition energies is the same as that observed for 0–0 transition energies, the “best” parameter set A as well as the sets B and C predict the wrong order.

In the higher energy region, our spectral analysis is generally much less conclusive². The calculations predict that some of the forbidden transitions expected in this region for naphthalene itself have allowed counterparts in *I–III*. This would be in agreement with our tentative assignments. The onset of the strong absorption is predicted quite correctly. In *II*, however, the calculated separation of the two strong bands is 2500 cm^{-1} , while experimentally, it is close to zero. The calculated and observed polarizations are in agreement. The third transition in both *I* and *III* is relatively much less intense than calculated. The large number of intense transitions predicted in the $45000\text{--}50000\text{ cm}^{-1}$ region for *III* agrees with the totally unresolved shape of the absorption curve in this region.

It is interesting to note that the approximate orbital pairing property expected¹⁸ to hold for the naphthalene analogue of borazine, which satisfies Koutecký's conditions, is indeed found: the symmetry of orbital energies holds within 0.03 eV and the equality of the absolute value of “paired” coefficients to better than 0.02. As a result, the first transition has an almost vanishing oscillator strength. The calculated electronic spectrum of this molecule is almost identical with that of naphthalene except that all excitations energies are higher. As in naphthalene, the first excited singlet (L_b ,

TABLE II
Analogues of Phenanthrene (*IX*)^a

Positions		Excited Singlets										
B	N		1	2	3	4	5	6	7	8	9	10
None		ΔE	30.3	33.9	39.6	40.7	41.1	43.6	46.1	48.2	49.5	
		f	0	0.44	0	0.58	1.44	0	0.38	0	0	
		φ	—	90	—	0	90	—	0	—	—	
10 (<i>IV</i>)	9	ΔE	30.9	35.5	37.0	40.9	43.8	44.0	46.0	48.7	49.5	
		f	0.21	0.03	0.05	1.33	0.49	0.33	0.17	0.21	0.16	
		φ	97	40	178	86	165	25	148	57	114	
10a (<i>V</i>)	4a	ΔE	31.2	32.0	38.4	39.8	41.7	42.2	45.0	47.2	48.5	
		f	0.03	0.09	1.24	0.47	0.70	0.08	0.02	0.21	0.07	
		φ	67	122	83	152	47	116	140	151	43	
4a	10a	ΔE	30.7	32.0	39.0	40.1	41.4	42.4	44.5	46.6	48.8	
		f	0.20	0.07	0.47	1.22	0.16	0.47	0.04	0.25	0.02	
		φ	121	99	43	92	63	16	136	129	2	
4b	4a	ΔE	25.3	27.3	31.2	33.6	38.7	42.4	45.2	45.3	47.8	49.6
		f	0.29	0.007	0.22	0.78	0.27	0.08	0.26	0.63	0.01	0.14
		φ	85	145	0	91	170	100	153	87	169	94
4b, 9, 10a	4a, 8a, 10	ΔE	30.7	34.0	37.0	40.7	44.6	45.5	47.2	49.3		
		f	0.18	0.17	0.62	0.36	0.12	0.49	0.07	0.01		
		φ	91	91	11	96	86	105	1	156		

^a See footnotes in Table I.

long-axis polarized) is represented by almost equal contributions from the $1 \rightarrow -2$ and $2 \rightarrow -1$ excited configurations; the second state (" L_a ", short-axis polarized) by the $1 \rightarrow -1$ configuration, the third state (" B_b ", long-axis polarized), again by the $1 \rightarrow -2$ and $2 \rightarrow -1$ configurations. A similar situation is also found for 4,8a,1,4a-diboradiazaronaphthalene (listed in Table I as B: 5,8a, N: 4a,8) where, however, the first rather weak band should be polarized along the short axis. The $1 \rightarrow -2$ and $2 \rightarrow -1$ configurations also mix considerably in 4,5,8a,1,4a,8-triboratriazaronaphthalene, benzoborazine, and 3,2-borazaronaphthalene, but in these cases the resulting state is not lowest but second in energy. The oscillator strength is again rather weak

TABLE II
(Continued)

IP	q_B	q_N	$P_{BN}(P_{CC})$
8-02, 8-48 9-57, 10-08 10-75, 11-96			
7-99, 8-56 9-40, 10-08 10-81, 11-99	0-387	1-562	0-602 (0-805)
8-03, 8-64 9-30, 10-53 10-70, 12-09	0-538	1-391	0-490 (0-569)
7-99, 8-34 9-50, 9-88 10-93, 12-15	0-528	1-382	0-488 (0-569)
7-65, 8-00 9-63, 10-71 10-98, 11-65	0-582	1-321	0-402 (0-434)
7-94, 8-51 9-78, 10-08 10-58, 12-19	(4b) 0-532 (9) 0-417 (10a) 0-538	(4a) 1-420 (8a) 1-416 (10) 1-568	(4a, 4b) 0-374 (0-434) (4b, 8a) 0-500 (0-569) (8a, 9) 0-409 (0-472) (9, 10) 0-650 (0-805) (10, 10a) 0-427 (0-472) (10a, 4a) 0-495 (0-569)

and in the latter two cases the polarization is along the short axis. The lowest excited state is represented by the $1 \rightarrow -1$ configuration. This is also the case for all other molecules in Table I except 1,2-borazaronaphthalene where the $1 \rightarrow -1$ state is second and the lowest state is represented by the $1 \rightarrow -2$ configuration which barely mixes with $2 \rightarrow -1$ at all. Such an uncoupling is actually the rule rather than the exception, the first two transitions having similar oscillator strength, and the cases enumerated above are the only ones where it does not occur. When it occurs, the state represented by the $1 \rightarrow -2$ configuration is usually below the " $2 \rightarrow -1$ " state and mostly second after the " $1 \rightarrow -1$ " state. Only in the 2,1-borazaro and 8a,1-borazaro

analogues of naphthalene the "2 \rightarrow -1" state rather than the "1 \rightarrow -2" state corresponds to the second excited state.

Similar regularities can be found in results for B,N-analogues of other alternant hydrocarbons. It would be interesting to deduce general rules, *e.g.* by the technique used by Koutecký¹². However, such a treatment is beyond the scope of this communication.

Analogues of phenanthrene (Table II, Figs 4 and 5). Up to 45000 cm^{-1} , the spectrum of phenanthrene contains at least five separate transitions: a weak band starting at 29000 cm^{-1} with an electronic transition moment polarized along the short axis (L_b), a long-axis polarized medium-intensity band starting at 34000 cm^{-1} (L_a) and a short-axis polarized one starting at 38000 cm^{-1} , a very strong long-axis polarized band at 40000 cm^{-1} and a medium-intensity short-axis polarized band at 45000 cm^{-1} (for a recent summary of evidence see ref.¹⁹). The spectrum is in good agreement with PPP calculations (Table II). Two additional forbidden bands are predicted above 39000 cm^{-1} (Table II); their presence has not been verified so far.

Results for *IV* are shown in Fig. 4. The position and relative intensity of the first transition are predicted quite well. However, the assignment of the following two weak calculated transitions is not obvious. The calculated relative intensities are unreliable since they are sensitive to the choice of parameters. Disregarding these

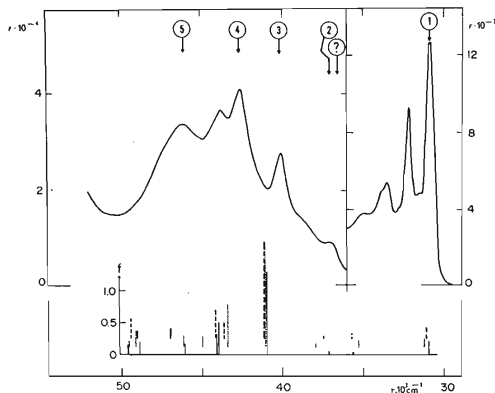


FIG. 4

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

As in Fig. 1.

intensities, one would be tempted to assign the second calculated transition to the second experimental band and the third transition to the third experimental band, starting at 39600 cm^{-1} , 2600 cm^{-1} higher than calculated. The calculated very intense transition at 41 kK would then correspond to the fourth experimental band, the strongest in the spectrum, higher calculated transitions would be associated with the following observed bands and shoulders. The main shortcomings of this assignment are the 2600 cm^{-1} error for the third excited state and a quite poor agreement for relative intensities. Unfortunately, the latter is unavoidable for any assignment: the prediction that a band near 41000 cm^{-1} should be much stronger than any other is independent of the choice of parameters, while experimentally in this region no one band seems substantially stronger than others. The other possibility would be to assume that only two of the first three calculated weaker transitions are actually observed experimentally (perhaps the strange unassigned weak shoulder² at 36500 cm^{-1} indicated with a question mark is to be associated with the third one). This assumption is in somewhat better agreement with calculated intensities for these bands. The calculated very strong fourth transition would then be associated with the third observed band, *etc.* While such an assignment gives better agreement for energies, maximum deviation being 1800 cm^{-1} (for the fourth observed band), the agreement for intensities in the high-energy region is even poorer than before.

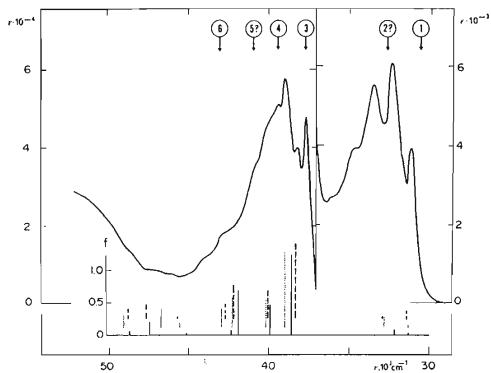


FIG. 5

10a,4a-Borazarophenanthrene (V)

As in Fig. 1.

In conclusion, agreement for *IV* is much less satisfactory than that for the other six molecules. This could perhaps be due to our complete neglect of bond length variation; the bonds between carbons and heteroatoms could be longer in *IV* in which the heteroatoms do not participate in conjugation as much.

Results of calculations for *V* are rather similar to those for phenanthrene, except that the first band is no longer of zero intensity. The ratio of intensities of the first two bands is sensitive to the choice of parameters and no reliable prediction is possible. The same is true of the transitions calculated at 40000, 41500, and 42000 cm^{-1} . Experimentally (Fig. 5), the spectrum is indeed analogous to that of phenanthrene, the first weak band is missing, the phenanthrene 38000 cm^{-1} and 40000 cm^{-1} bands are now better resolved because they have more comparable intensities (third and fourth transitions in *V*, see 4,5-methylenepheneanthrene for a similar resolution²⁰) and the shoulder at 41000 cm^{-1} (fifth indicated transition) possibly corresponds to an independent transition where none is observed in phenanthrene. The tentative conclusion from experimental data was that the first poorly resolved band probably originates from two independent transitions². If this is accepted, and if the shoulder at 41000 cm^{-1} is assigned as an independent transition, the agreement with calculations is perfect, except for the uncertainties in intensities of some of the bands as mentioned above. The existence of a region of low absorption near 45000 cm^{-1} and the presence of bands of medium intensity at somewhat higher energies also agree well.

TABLE III

Transition Moment Directions in 10a,4a-Borazarophenanthrene (*V*)

Transition	1	2	3	4	5 ^a	6 ^a
	Experimental ^c					
$ \varphi ^b$	54–90	(20–50)	0–40	46–83	40–90	40–66
Most probable values of $ \varphi $	54–73	uncertain	19–40	46–68	40–74	40–66
	Calculated ^d					
A	23	32	7	62	43	26
B	5	39	2	78	42	2
C	40	9	5	67	14	60

^a The peak labelled 5 in Fig. 5 may belong to the fine structure of transition 4. In such a case the first two entries in column 5 would have to be replaced by 40–66 (from column 6). ^b $|\varphi|$ is the deviation from the *y* axis in degrees (formula IX, Chart I). ^c Cf. ref.². ^d Using parameter sets A, B, C, (see text). Set A is the "best" set used in the other tables.

If our tentative identification² of the 0-0 bands of individual electronic transitions in the spectrum of *V* is correct, the purely electronic components of the transition moments have directions deviating from the long (*y*) axis by amounts indicated in Table III. A comparison with calculated values is a rather demanding test of the quality of wavefunctions. The poor agreement obtained, particularly for the first transition, clearly shows the limitations of the present calculations (Table III). First of all, the remark already made for calculated relative intensities is even more applicable to polarization directions: for some transitions, small changes in parameters have large effects. A closer inspection of results of additional calculations shows that this is the case when a gradual change in the effective electronegativity of the heteroatoms brings two or more excited states of the PPP model through an avoided crossing. While energies are barely affected, the wavefunctions change drastically. Unfortunately, such avoided crossings frequently occur in the neighborhood of the optimum parameter values. In our parameter study, we attempted to take this into account by including the relative intensities of the first two transitions in *I* among the values to be fitted. However, already the difference in effective electronegativity due to the absence of a methyl substituent on the boron atom, and bonding to two aromatic carbons instead, neglected in our work, could make a large difference.

In view of the sensitivity of polarization directions of transitions 1 and 2 to parameter choice a comparison with experiment is virtually meaningless. At any rate, agreement is very poor for transition 1. Results for intense transition 3 and 4 are much less sensitive to parameter choice and agree with experimental data, while transitions 5 and 6 again present problems.

In summary, it seems highly desirable to obtain additional and more accurate experimental data on polarization of transitions in molecules of low symmetry. At present, they provide the ultimate test for spectral calculations on such molecules. There are some indications²¹ that the standard PPP method is capable of giving good results; the case of *V* is the worst we have encountered so far. In view of this, predicted polarization directions in other unsymmetrical borazaro molecules are probably meaningful only for strong transitions.

Table II also contains predictions for several additional analogues of phenanthrene.

Analogues of triphenylene (Table IV, Figs 6 and 7). The absorption spectrum of triphenylene^{22,23} starts off with two symmetry-forbidden bands at 29 300 cm⁻¹ and 34 500 cm⁻¹ followed by an intense allowed transition into an *E'* state at 38 800 cm⁻¹. Absorption is very weak between 42 000 and 48 000 cm⁻¹ and then increases again due to the presence of additional strong transitions at 50 400 cm⁻¹ and 52 600 cm⁻¹. The agreement with PPP calculations (Table IV) is quite good, assuming that a forbidden transition predicted at 37 400 cm⁻¹ and a very weak transition at 43 200

TABLE IV
 Analogues of Triphenylene (X)^a

Positions		Excited singlets										
B	N		1	2	3	4	5	6	7	8	9	10
None		ΔE	29.9	34.4	37.4	37.4	39.5	39.5	43.2	43.2	47.8	47.8
		f	0	0	0	0	1.76	1.76	0.05	0.05	0	0
		φ	—	—	—	—	0	90	0	90	—	—
12b (VI)	4a	ΔE	30.6	31.7	36.8	38.1	38.8	40.8	42.1	42.6	45.3	45.9
		f	0.07	0.07	0.04	1.07	1.27	0.27	0.16	0.14	0.01	0.02
		φ	45	76	171	77	163	69	105	35	55	96
4b, 8b, 12b (VII)	4a, 8a, 12a	ΔE	(29.4)	34.8	36.2	36.2	39.7	39.7	42.2	42.2	46.6	47.3
		f	0	0	1.14	1.14	0.02	0.02	0.003	0.003	0	0.08
		φ	—	—	0	90	0	90	0	90	—	0
8a	8b	ΔE	23.6	24.9	29.0	32.8	34.9	36.1	37.8	39.9	41.4	41.9
		f	0.35	0.07	0.15	0.32	0.19	0.97	0.27	0.08	0.26	0.23
		φ	86	107	0	90	20	177	98	163	11	92

^a See footnotes in Table I.

cm^{-1} are not noticed in the spectrum due to the presence of the very strong transition at $38\,800\text{ cm}^{-1}$ (observed, $39\,500\text{ cm}^{-1}$ calculated). The forbidden transitions predicted near $48\,000\text{--}49\,000\text{ cm}^{-1}$ could be responsible for the unresolved rise of absorption in this region. The calculated spectrum of VI (Fig. 6) starts with three bands of medium intensity. The first strong transition should be blue shifted by $1\,900\text{ cm}^{-1}$ with respect to VII (Fig. 7) and split into two. Several weaker transitions should follow, then a region of very low absorption, then a fairly strong band about $2\,000\text{ cm}^{-1}$ lower than in VII. Experimentally, only two of the expected three transitions have been detected² in the low-energy region. It is possible but by no means certain that three are actually present and happen to overlap badly enough to escape detection. For example, the two peaks assigned² as vibrational components of the second transition in Fig. 6 could correspond to two separate transitions in reality. Another possibility is that the third calculated band is hidden under the strong absorption due to the peak at $37\,100\text{ cm}^{-1}$. At any rate, while the calculated energy of the first transition agrees perfectly, the second and third transitions are probably wrong by $2\,000\text{--}3\,000\text{ cm}^{-1}$, and one of them is perhaps not present at all. As predicted, the very strong transition is blue shifted compared with VII (by $2\,300\text{ cm}^{-1}$). Its more complicated and irregular shape makes it likely but not certain that it is indeed split into two and that additional ones follow at higher energies. Also the

TABLE IV
(Continued)

Excited singlets				IP	q_B	q_N	$p_{BN}(p_{CC})$
11	12	13	14				
48.4	48.6			8.20, 8.20			
0	0			8.92, 10.00			
—	—			10.00, 10.21			
47.1	48.6	49.4		7.99, 8.32	0.516	1.405	0.498 (0.585)
0.01	0.41	0.07		9.11, 9.52			
63	169	64		10.15, 10.50			
47.3	48.5			8.16, 8.16	0.547	1.402	(4a, 4b) 0.347 (0.391)
0.08	0			8.97, 10.22			(4b, 8a) 0.516 (0.585)
90	—			10.22, 10.25			
44.5	46.5	47.1	48.9	7.34, 7.97	0.613	1.288	0.373 (0.391)
0.001	0.04	0.06	0.02	9.02, 9.70			
60	124	66	70	10.65, 10.85			

presence of a quite strong peak at 48000 cm^{-1} in *VI* where there is none in *VII* is in agreement with calculations.

The calculated spectrum of *VII* (Fig. 7) is almost exactly like that of triphenylene, except that the strongly allowed third transition should be less intense and red-shifted by 3300 cm^{-1} , and that most of the transitions which have zero oscillator strengths in the hydrocarbon should have non-vanishing though very small oscillator strengths in *VII*. The agreement of the two experimental spectra is indeed striking; the red shift of the now less intense strong transition is 3900 cm^{-1} . There seem to be only a few other differences: the strong allowed band is broader in the spectrum of *VII*, which could be due to the fact that two weak bands in this region, of zero intensity in the hydrocarbon, should be weakly allowed in *VII*. Further, in *VII* the second transition is red-shifted by 1850 cm^{-1} compared to the hydrocarbon, if our tentative analysis is correct. The calculated shift is however 400 cm^{-1} in the opposite direction. The first transition is one of the total of three in the spectra of *I-VII* which were chosen for parameter fitting and therefore the reasonable agreement of its energy with experiment is trivial. As a matter of fact, for the "best" values of parameters it is predicted to be 500 cm^{-1} lower than the first transition in triphenylene, in reality it is 1300 cm^{-1} higher. On the whole, the agreement for *VII* is quite good considering the large number of heteroatoms present.

Analogues of benzene (XI, Table V). Borazine appears to be the only compound whose UV spectrum has been reported²⁴. This is probably the worst available molecule to test our calculations on because it is composed exclusively of heteroatoms. The spectrum (in heptane) starts with four poorly resolved weak peaks which seem to form a progression in 900 cm^{-1} . The first of these is located at 50100 cm^{-1} but if the assignment to a symmetry-forbidden transition is correct this is not the 0-0 band. The next band has a maximum at 58400 cm^{-1} , is very broad and structureless. Its high intensity suggests strongly that it is due to an allowed transition into a degenerate (E_1) excited state. By analogy with benzene and on basis of simple molecular orbital calculations it is generally believed that a second forbidden transition is hidden somewhere near 54000 cm^{-1} . The spectrum of B,B,B-trimethylborazine, with which our results should more properly be compared, is even more diffuse. The first band is seen only as an indistinct shoulder at about 52400 cm^{-1} , the intense band now has maximum at 56800 cm^{-1} . The agreement with our calculation is poor, and it is not much of a consolation that this is also true of most other calculations, even those which concentrate on borazine alone. The first transition is correctly predicted to be symmetry-forbidden but this is apparently the result of any π -electron calculation, and its energy is $8000-9000\text{ cm}^{-1}$ too low. The energy of the degenerate transition is about 3000 cm^{-1} too low. Like all other π -electron calculations, we obtain one additional forbidden transition between the two, but meaningful comparison with experiment is impossible. The agreement can be improved somewhat by parameter adjustments without affecting agreement for other molecules. However, we have not

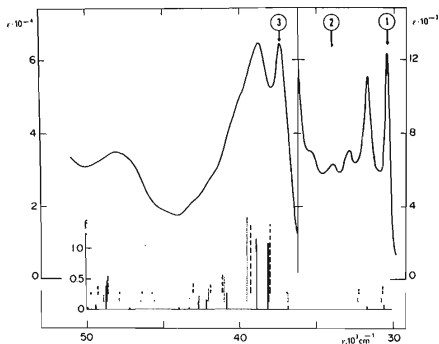


FIG. 6

12b,4a-Borazarotriphenylene (VI)

As in Fig. 1.

TABLE V
Analogues of Benzene (XI)^a

Positions		Excited singlets				IP	q_B	q_N	$p_{BN}(p_{CC})$
B	N	1	2	3	4				
None		ΔE 38.4	48.4	55.0	55.0	9.23, 9.23			
		f 0	0	1.17	1.17	12.15			
		φ --	--	0	90				
1	2	ΔE 36.7	46.0	54.3	58.5	8.40, 9.84	0.462	1.470	0.562 (0.667)
		f 0.25	0.04	1.09	0.56	12.33			
		φ 97	112	13	110				
1, 4	2, 5	ΔE 29.9	49.6	54.9	60.2	7.58, 10.66	0.547	1.393	0.575 (0.667)
		f 0.48	0.01	0.99	0	12.17			
		φ 95	133	7	--				
1, 5	2, 4	ΔE 32.4	42.5	52.6	62.0	7.93, 9.86	0.485	1.454	0.473 (0.667)
		f 0.27	0.01	1.08	0.30	13.05			
		φ 90	0	0	90				
1, 3	2, 6	ΔE 39.0	47.5	52.4	57.0	8.49, 9.60	(1) 0.454	(2) 1.532	(23) 0.556 (0.667)
		f 0.25	0.04	0.54	0.71	12.09	(3) 0.411	(6) 1.542	(12) 0.586 (0.667)
		φ 81	25	175	89				(16) 0.547 (0.667)
1, 3, 5 6	2, 4, (borazine)	ΔE 43.0	52.8	54.0	54.0	9.14, 9.14	0.419	1.581	0.553 (0.667)
		f 0	0	0.67	0.67	11.22			
		φ --	--	0	90				

^a See footnotes in Table I.

TABLE VI
Analogues of Anthracene (XII) and Pyrene (XIII)^a

Positions		Excited Singlets									
B	N		1	2	3	4	5	6	7	8	9
None (anthracene)		ΔE	27.8	29.3	37.0	37.7	40.0	40.7	43.7	47.8	49.4
		f	0.36	0	0	0	2.78	0	0	0.01	0
		φ	90	—	—	—	0	—	—	90	—
9a	4a	ΔE	26.3	28.6	35.3	36.5	39.1	40.1	44.4	45.1	48.4
		f	0.25	0.03	1.17	0.04	0.42	0.25	0.35	0.93	0.17
		φ	101	155	7	87	11	122	50	164	83
8a, 9a, 10	4a, 9, 10a	ΔE	29.9	30.3	36.3	39.4	41.7	45.0	45.7	46.2	48.8
		f	0.32	0.005	0.49	0.38	0.17	1.39	0.05	0.06	0.02
		φ	90	0	0	90	0	0	90	90	90
None (pyrene)		ΔE	28.0	28.6	35.5	35.7	38.8	40.9	41.8	44.1	44.5
		f	0	0.86	0	0	1.01	0	0	0	0
		φ	—	90	—	—	0	—	—	—	—
10c	10b	ΔE	21.9	26.1	29.6	34.7	39.0	40.8	41.5	42.1	43.4
		f	0.004	0.40	0.37	1.64	0.06	0.37	0.31	0.12	0.002
		φ	0	90	0	90	0	0	90	0	90

^a See footnotes in Table I.

used borazine spectrum for parameter fitting, for several reasons: *a*) we have been trying to keep the number of pieces of data used for this purpose to minimum, *b*) because of the abundance of heteroatoms, the bonding conditions in borazine are not really typical of those in most borazaro aromatic compounds, *c*) the spectrum of borazine is too diffuse and reliable assignments are hard to make.

Results for other borazarobenzenes presented in Table IV are presumably the more reliable the fewer heteroatoms the molecule contains.

Analogues of anthracene (XII) and pyrene (XIII) (Table VI). Spectra of the borazaro analogues of these hydrocarbons should look much more complicated than those of the parents because several transitions presumably present but forbidden and unobserved in the hydrocarbons should be quite strongly allowed in the heterocycles. If this is indeed the case, one would feel more confident in claiming that the forbidden transitions are actually present in the spectra of the parent hydrocarbons as calculated. 10c,10b-Borazaropyrene seems interesting because of the large predicted red shift of the first weak band compared to the L_b band of pyrene.

TABLE VI
(Continued)

Excited Singlets			IP	q_B	q_N	$P_{BN}(P_{CC})$
10	11	12				
50.1			7.46, 9.01			
0.38			9.25, 10.43			
90			10.45, 12.06			
			7.50, 8.57	0.582	1.331	0.448 (0.502)
			9.53, 10.13			
			10.79, 12.26			
			7.69, 8.51	(8a) 0.528	(9) 1.594	(8a, 9) 0.509 (0.611)
			9.85, 10.09	(10) 0.382	(10a) 1.434	(8a, 10a) 0.453 (0.502)
			10.42, 12.29			(10, 10a) 0.493 (0.611)
44.9	49.5		7.46, 8.69			
1.41	0		9.28, 9.83			
90	—		10.25, 11.51			
44.5	45.9	46.3	7.44, 7.96	0.556	1.356	0.456 (0.510)
0.0001	0.06	0.03	9.61, 9.91			
90	0	90	10.63, 11.73			

Analogues of acenaphthylene (XIV, Table VII). Simple PPP calculations using parameters identical to ours underestimate somewhat the excitation energy of the first transition in this hydrocarbon²⁵; this will probably also be true for the heterocycles. The predicted difference in the energies and intensities of the transitions in 5a,8b- and 8b,5a-borazaro derivatives is striking. It is very probably real and would be rather interesting to explore.

Analogues of cyclohepta[de]naphthalene (XV, Table VIII). As in acenaphthylene, the calculated energies of the first band are probably a little too low²⁵. Some striking differences between isomers are again predicted.

Structure of the condensation product of 8a,4a-borazaronaphthalene (II) with 1,1,3,3-tetraethoxypropane. Dewar and Jones²⁶ observed formation of an intense violet coloration (absorption peak with maximum at 19500 cm^{-1}) when II reacted with 1,1,3,3-tetraethoxypropane in an acidic medium and proposed structure XVI for the product, which could not be isolated.

TABLE VII
Analogues of Acenaphthylene (XIV)^a

Positions		Excited Singlets									
B	N		1	2	3	4	5	6	7	8	9
None		ΔE	22.1	30.3	30.9	38.3	44.8	47.6	47.8	50.0	
		f	0.04	0.31	0.22	0.005	1.21	0.005	0.004	0.006	
		φ	0	90	0	90	0	0	90	90	
2	1	ΔE	24.4	31.2	33.3	39.1	45.4	46.1	49.5	50.0	
		f	0.08	0.09	0.19	0.42	0.53	0.62	0.35	0.04	
		φ	62	49	99	5	13	160	22	139	
5a	8b	ΔE	28.0	28.2	30.8	41.2	43.2	47.5	48.4	49.7	
		f	0.50	0.14	0.05	0.84	0.24	0.78	0.10	0.35	
		φ	0	90	0	90	0	0	90	0	
8b	5a	ΔE	15.3	28.4	32.5	37.8	42.3	43.1	45.8	47.6	48.5
		f	0.01	0.02	0.19	0.78	0.02	0.12	1.58	0.31	0.05
		φ	0	90	0	90	0	90	0	90	0

^a See footnotes in Table I.

Our calculation for XVI gave the following results for excitation energies in $\text{cm}^{-1} \cdot 10^{-3}$ and oscillator strengths (in parentheses): 12.2 (0.008), 27.4 (0.4), 29.2 (0.5), 38.3 (0.9), 42.3 (0.6), etc., in complete disagreement with the experimental observation. Even allowing for the fact that XVI is a somewhat unusual charged species, the discrepancy is remarkable in comparison with the kind of agreement obtained for molecules I–VII. Moreover, for another analogue of phenalene, XVII, the agreement is quite reasonable: calculated ($\text{cm}^{-1} \cdot 10^{-3}$, f) 28.2 (0.05), 29.8 (0.47), 32.9 (0.16), 42.4 (0.04), 44.1 (1.1), etc., experimental $\text{cm}^{-1} \cdot 10^{-3}$, $\log \epsilon$, as estimated from a published figure²⁷, assignment of overlapping individual transitions is not clearcut) 27.4 (4.0), 30.3 (4.0), 32.6 (3.8), 42.2 (4.5).

Since the assignment²⁶ of structure XVI to the colored reaction product was only tentative and not based on a rigorous structure proof, we have looked for other plausible candidates for reaction products. A calculation for the 2 : 1 condensation product, the cyanine dye XVIII, gave the following excitation energies in $\text{cm}^{-1} \cdot 10^{-3}$ (oscillator strengths): 17.4 (1.5), 20.3 (0.09), followed by a few very weak transitions, then 35.6 (0.1), 36.6 (0.2), 40.9 (0.1), 42.6 (1.3), etc., in a much more acceptable agreement with the position of the observed first peak. It seems that the structure of the condensation product quite likely is XVIII rather than XVI and we hope to obtain experimental evidence on this point.

TABLE VII
(Continued)

IP	q_B	q_N	$p_{BN}(p_{CC})$
8·10, 8·54 9·11, 11·12 11·25, 13·17			
7·85, 8·87 9·09, 10·90 11·44, 13·20	0·373	1·617	0·601 (0·845)
8·10, 8·73 9·59, 10·79 11·44, 13·70	0·573	1·410	0·450 (0·548)
7·37, 8·67 9·21, 11·30 11·37, 13·34	0·569	1·380	0·510 (0·548)

Energies of the lowest triplet states. Calculations using the Mataga approximation for electron repulsion integrals are well known to give too low energies for the lowest triplet state (*e.g.*, ref.²⁸). Our calculations give 16600 cm^{-1} for naphthalene, 19200 cm^{-1} for phenanthrene, to be compared with the experimental values^{29,30} 21200 cm^{-1} and 21600 cm^{-1} , respectively. Phosphorescence measurements have been reported² for *I-IV*; the 0-0 peaks lie at 23600 , 22700 , 23000 , and 23800 cm^{-1} , respectively. The calculated values are 21400 , 17600 , 19400 and 23100 cm^{-1} , respectively. The calculated shifts with respect to the parent hydrocarbons thus have correct signs and even acceptable relative magnitudes but are overestimated by about a factor of two.

IONIZATION POTENTIALS

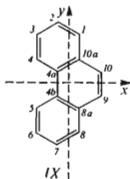
Dewar and collaborators¹¹ have determined eight successive ionization potentials of *II* by photoelectron spectroscopy and suggested tentative assignments. A comparison with naphthalene (Table IX) shows a striking similarity except that the second IP of naphthalene ($8\cdot79\text{ eV}$) has no observed counterpart in *II*. Two additional differences are noticed at higher energies, where the IP's at $14\cdot05$ and $16\cdot74\text{ eV}$ in *II* have no analogy in naphthalene. Many dozens of calculations with widely varying para-

meters for heteroatoms (five examples are shown in Table IX) all lead to the same conclusion: the coincidence of π -levels of naphthalene and *II* ought to be complete, contrary to the tentative suggestion of Dewar and collaborators¹¹. We suggest that their photoionization spectrum does not show the second IP, which according to our



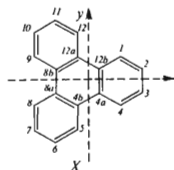
VIII

I, 2 = B, 1 = N
II, 8a = B, 4a = N
III, 4 = B, 3 = N, 2 = N(aza)

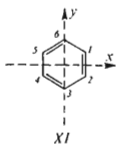


IX

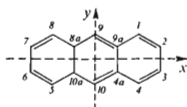
IV, 10 = B, 9 = N
V, 10a = B, 4a = N



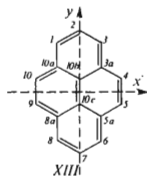
VI, 12b = B, 4a = N
VII, 4b = 8b = 12b = B,
 4a = 8a = 12a = N



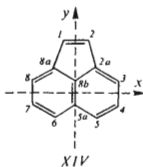
XI



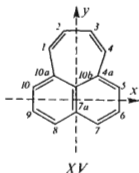
XII



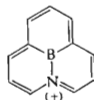
XIII



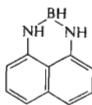
XIV



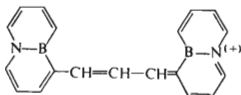
XV



XVI



XVII



XVIII

CHART I

results should be rather close to the first one. Depending on the parameters, they can be degenerate or separated by as much as approximately 1 eV. However, in either case, assignment of the second calculated to the second observed (10.07 eV) IP results in poor agreement and moreover destroys the otherwise quite good agreement of the calculated third and fourth IP's with the observed second and third IP's. Using the "best" parameters (set A) the second IP is predicted only 0.3 eV above the first IP. The agreement of the calculated first IP with the observed value is a consequence of the fitting of values of γ_B and γ_N . Table IX shows that other parameter values have very little effect. This is easily understood since the highest occupied molecular orbital has a nodal plane going through the B and N atoms¹¹. The fair agreement of calculated with experimental IP's encouraged us to include predictions for the lower π -levels in Tables I, II, and IV – VIII.

The IP of borazine has been recently redetermined by the electron impact method³¹ and is now believed to be 0.22 ± 0.1 eV higher than that of benzene, while the IP of B,B,B-trimethylborazine is 0.25 ± -0.1 eV below that of benzene. Surprisingly enough, these values are in excellent agreement with our result (0.1 eV below benzene). Our parameters seem to give only the correct order of magnitude for the IP of borazaroethylene (9.27 eV as compared for example with the reported¹¹ value for 10,9-borazarodecaline, 8.47 eV).

ELECTRON DISTRIBUTION

Our parameters have not been optimized for ground state properties and are thus likely to reproduce such properties only in a relative sense, if at all. Fortunately, it seems that our "best spectral" set A is not far off even on the absolute scale since the π -electron densities predicted for boron, whose values are quite sensitive to the effective electronegativities of the heteroatoms, seem to be of the right order of magnitude. Silver and Bray³⁴ estimate from measurements of quadrupole coupling constants that about 0.45 of an electron is on the average donated from nitrogen to the boron atom in boron nitride, the borazaro analogue of graphite. The π -electron density on the 8a boron atom in the pentaborapentazaro analogue of naphthalene (VIII, Table I), which comes closest to this bonding situation, is calculated to be 0.50. Similar values for π -electron densities also resulted from all-valence-shell-electron calculations¹.

¹¹B NMR chemical shifts. In otherwise similar environments ¹¹B NMR chemical shifts seem to be dominated by the degree of occupancy of the boron $2p_z$ orbital (see ref.⁸ for a more detailed discussion). For borazaro analogues of planar conjugated hydrocarbons, this leads one to expect increased shielding as the π -electron density on boron q_B increases. The ¹¹B NMR shifts have been reported⁸ for I–IV and VI. We find a very good linear relation between the ¹¹B chemical shift for these compounds and the calculated q_B 's for all parameter sets tested in spite of the wide differences

TABLE VIII
Analogues of Cyclohepta[de]Naphthalene (XV)^a

Positions											
B	N		1	2	3	4	5	6	7	8	9
None	ΔE	18.9	27.3	30.3	36.2	41.5	42.0	43.6	44.9	45.1	
	f	0.06	0.43	0.12	0.005	0.12	0.53	1.12	0.07	0.04	
	φ	0	90	0	90	0	90	0	0	90	
2	3	ΔE	11.6	25.5	28.0	30.5	33.3	39.5	40.5	43.2	44.8
	f	0.09	0.33	0.11	0.10	0.34	0.02	0.89	0.65	0.03	
	φ	164	101	17	160	36	160	83	164	163	
3	4	ΔE	21.7	29.5	30.8	38.2	39.5	42.4	44.5	44.9	47.4
	f	0.08	0.31	0.11	0.32	0.69	0.09	0.28	0.35	0.47	
	φ	54	78	147	168	92	28	161	169	33	
4	3	ΔE	23.8	27.1	30.8	39.4	41.5	42.3	44.2	45.3	46.8
	f	0.04	0.61	0.05	0.25	0.33	0.16	0.43	0.07	0.31	
	φ	168	87	13	5	174	7	4	28	69	

^a See footnotes in Table I.

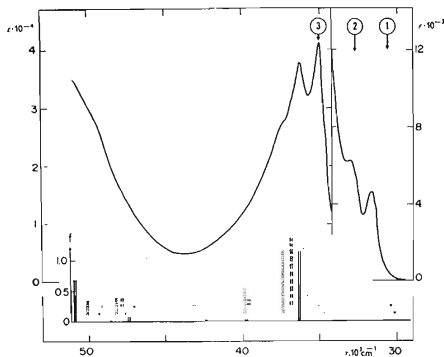


Fig. 7

4b,8b,12b,4a,8a,12a-Triboratriazarotriphenylene (VII)
As in Fig. 1.

TABLE VIII
(Continued)

			IP	q_B	q_N	$\rho_{BN}(\rho_{CC})$
10	11	12				
47.3	48.8		6.97, 9.07			
0.84	0.43		9.66, 9.80			
90	0		11.42, 11.53			
46.0	47.4	50.8	6.49, 9.00	0.531	1.348	0.442 (0.463)
0.24	0.01	0.91	9.23, 10.07			
85	170	42	11.15, 12.19			
48.3	49.9		7.23, 9.20	0.368	1.572	0.590 (0.819)
0.64	0.49		9.37, 10.01			
61	138		11.32, 11.75			
49.6			6.95, 8.94	0.348	1.566	0.578 (0.819)
0.19			9.18, 9.99			
16			11.11, 11.77			

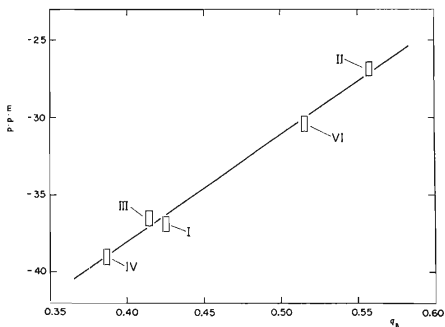


FIG. 8
 ^{11}B NMR Chemical Shifts of Borazaro Heterocycles in Benzene (Boron Trifluoride Etherate Standard) Plotted against π -Electron Densities on Boron calculated Using Parameter Set A (q_B)

in the actual values of q_B for different parameter sets. The deviations from linearity are comparable to experimental error. Thus, calculations using any of these sets can be used to predict ^{11}B NMR shifts for additional molecules by interpolation and possibly even extrapolation. The results for *III* were very little sensitive to the choice of parameters for the aza nitrogen.

The estimated error of experimental values is ± 0.5 p.p.m., the use of different solvents for different molecules adds another uncertainty of similar magnitude; the total range covered is 12 p.p.m. Values of q_B obtained with parameter set A are given in Tables I, II, IV–VIII. For this parameter choice, regression line for the five points available (Fig. 8) is given by the formula

$$^{11}\text{B chem shift (p.p.m.)} = 69.1q_B - 65.7,$$

valid for boron trifluoride etherate standard and benzene solvent (chemical shifts of *I* and *II*, reported in carbon disulfide and acetic acid, were converted to benzene values by adding 0.6 and 1.0 p.p.m., respectively, assuming that such solvent shifts are the same as for *VI* and *III*). The correlation coefficient is 0.996, the correlation is significant on 0.1% probability level. The largest deviation is 0.6 p.p.m., comparable with the total experimental uncertainty. It seems almost impossible that additional data for new molecules will also fit so well, particularly since we fail to distinguish between a methyl-substituted boron atom (such as in *I*) and a bridgehead boron atom (e.g., *II*) in our calculations. Moreover, it is likely that different regression lines will be required for chemical shifts of boron atoms in environments other than two carbon and one nitrogen neighbors. Data are available for three such cases. Our prediction for B-trimethylborazine would be -36.75 p.p.m.; values reported by various authors^{35–37} are -32.4 , -34.5 , -34.7 , and -34.9 to -36.1 (for B-trialkyl borazines). For borazine itself³⁵, the shift has been reported as -29.1 and -30.4 p.p.m. Our prediction for the B-tetramethyl derivative of the B–N analogue of naphthalene would be -31.1 p.p.m., for bridgehead boron, -37.0 for boron in the β position and -39.0 for the α -boron. A very broad unresolved band (half-width 19 p.p.m.) with maximum at -34.5 p.p.m. has been reported experimentally³⁷. For the unsubstituted BN analogue of naphthalene³⁶, the reported value for the bridgehead boron is -25.0 p.p.m., the two others give an unresolved peak with maximum at -30.0 p.p.m. Finally, our result for the B–N analogue of ethylene is $q_B = 0.314$. It is hard to say which actual molecule this should correspond to (perhaps B,B,N-trimethylborazine). The predicted chemical shift is -44.0 p.p.m. Experimental ^{11}B shifts are available³⁶ for a series of B-butyl-N,N-dialkyl-borazines: -42.4 to -43.9 p.p.m.

Thus, a fair agreement is obtained in all three cases. It seems that both the presence of more than one nitrogen adjacent to boron and replacement of its methyl substituent by hydrogen lead to an increased shielding. Further, it is worth pointing out

that the intercept of our regression line is of the correct order of magnitude: for $q_B = 0$, we expect a chemical shift of -65.7 p.p.m. In reality, no boron adjacent to nitrogen in a planar molecule will have $q_B = 0$, but rough comparison is provided by the values³⁶ for triphenylboron (-60.0 p.p.m.), trivinylboron (-55.2 p.p.m.) and trimethylboron (-86.3 p.p.m.).

"Aromaticity" and similarity to the parent hydrocarbons. Since our q_B values seem to provide a reasonable approximation to reality, they deserve a more detailed discussion. The value of q_B indicates to what extent boron participates in conjugation and consequently it could be considered a measure of the "aromaticity" of the borazaro compound. On basis of simple resonance theory arguments one could expect q_B to be largest if the heterocycle can be derived from the parent hydrocarbon by replacing two carbon atoms connected by a bond of very low π -bond order. Values of q_B and p_{CC} collected in Tables I, II, and IV to VIII confirm this fully; some extreme

TABLE IX
 π -Ionization Potentials

Naphthalene (VIII)									
Exp.	8.11	8.79	9.96	10.90	12.26 ^a	13.22		15.73 ^a	
Calc.	(8.11) ^b	9.09	10.12	11.07		12.88			
8a-4a-Borazonaphthalene (II)									
Exp.	8.24		10.07	10.95	12.23 ^a	13.07	14.05 ^a	15.53 ^a	16.74 ^a
Calc. A	(8.27) ^c	8.63	10.29	11.19		13.25			
Calc. B	(8.27) ^c	8.87	10.17	11.22		13.22			
Calc. C	(8.30) ^c	8.58	10.15	11.20		13.12			
Calc. D ^d	(8.26) ^c	9.34	10.32	11.29		13.19			
Calc. E ^d	8.47	8.75	9.90	11.36		12.50			

^a Assigned to levels of σ symmetry. ^b Ionization potentials (in eV) were calculated from SCF orbital energies by adding 1.428 eV, then multiplying by -1 . The value 1.428 eV was chosen so as to reproduce exactly the first IP of naphthalene; it also leads to good values for the first photoionization potential of other aromatic hydrocarbons: benzene (9.23 eV, exp. 9.24 eV), anthracene (7.46 eV, exp. 7.38 eV), and azulene (7.44 eV, exp. 7.41 eV). Such a procedure amounts to a calculation of differences of IP's only³². The ionization potential of the methyl radical (9.84 eV) is sometimes used as reference³³; our result for it is 9.99 eV. For origin of quoted experimental IP's see ref.³³ ^c Used in fitting of parameters for B and N. ^d Sets D and E are examples of parameter sets more significantly differing from the "best" set A. D: $\beta_{CB} = \beta_{CN} = \beta_{BN} = -2.318$ eV, $I_{B-} = 6$ eV, $\gamma_B = 9.84$ eV, $A_{N+} = 6$ eV, $\gamma_N = 11.84$, E: $\beta_{CB} = \beta_{CN} = \beta_{BN} = -1.8$ eV, $I_{B-} = 3$ eV, $\gamma_B = 9$ eV, $A_{N+} = 6.5$ eV, $\gamma_N = 13.5$ eV.

cases not included there are *trans*-3,2-borazarobutadiene, $q_B = 0.644$, $q_N = 1.259$ ($p_{BN} = 0.411$, $p_{CC} = 0.373$), 1,1'-borazarobiphenyl, $q_B = 0.667$, $q_N = 1.232$ ($p_{CC} = 0.325$, $p_{BN} = 0.327$), 6b,6a-borazaroperylene, $q_B = 0.633$, $q_N = 1.265$ ($p_{CC} = 0.366$, $p_{BN} = 0.355$). Such compounds, in which the B—N pair is positioned across a classically single bond, would normally be classified as mesoionic ylides (the calculated π -electron components of dipole moments are 5.6 D, 8.2 D, 6.0 D, respectively). They are quite closely related to the mesoionic and so far unknown 1,3-borazaro heterocycles. Such compounds are highly "aromatic" in a limited sense of the word but they will probably not exhibit "aromatic stability" and should resemble other known ylides rather than the parent hydrocarbons. This should also be reflected in their electronic spectra; the first band of the three above-named molecules should be red-shifted by 16 100, 14 500 and 6 500 cm^{-1} , respectively, with respect to the parents. Other examples are shown in Tables II, IV, and VIII.

On the other end of the scale are compounds such as 1,2-borazaroacenaphthylene, $q_B = 0.373$, $q_N = 1.617$ ($p_{CC} = 0.845$, $p_{BN} = 0.601$), with a high double bond character in the B—N linkage, which thus forms a more or less self-contained entity interacting but little with the rest of the molecule ($p_{BC} = 0.342$, $p_{NC} = 0.392$), with a much smaller π -dipole moment (1.22D), and progressively less entitled to be called "aromatic" as the extreme is approached: borazaroethylene (borazene), $q_B = 0.314$, $q_N = 1.686$ ($p_{CC} = 1.000$, $p_{BN} = 0.728$). In such cases, the first bands in the electronic spectra should be blue-shifted compared with the parent hydrocarbons (Tables VII, VIII).

Molecules which should be "aromatic" and yet have a chance to be reasonably stable are found in the middle of the scale. Compounds I—VII all belong to these, IV clearly being the least "aromatic". Compounds of this group should bear most resemblance to the parent hydrocarbons, also in electronic spectra. The calculated π -electron components of the dipole moment should be relatively small (mostly 2—3 D). They are probably just about cancelled by the σ -electron components^{1,38-40}. Because of large uncertainties in the latter it seems unreasonable to try to predict total dipole moments on the basis of π -electron calculations.

The correlation of q_B with p_{CC} (and p_{BN}) is not perfect. For example, bridgehead boron atoms tend to have somewhat higher electron densities than expected, and the situation becomes more complicated for molecules with several adjacent N,B pairs.

π -Electron densities. Relative π -electron densities on carbon atoms have been estimated for II from proton NMR chemical shifts⁴⁰. In II (numbering as in VIII with B in 8a, N in 4a), the part of the chemical shift attributed to π -electron charge is 1.08 p.p.m. for proton in position 4, 0.84 for position 3, 0.30 for position 1, all upfield, and 0.10 downfield for proton in position 2. π -Electron densities calculated with parameter set A (B, C) are 1.062 (1.090, 1.084) in position 4, 1.019 (1.001, 1.018) in 3, 0.974 (0.941, 0.978) in 1 and 0.987 (1.002, 0.997) in 2. The "best" spectral

set A is in agreement with the experimental estimates except for the order of positions 1 and 2; sets B and particularly C give worse results, but they all agree that position 4, adjacent to nitrogen, has highest π -electron density.

Unfortunately, such data do not seem available for any other molecules. On the other hand, calculations with the "best" spectral parameter set might prove of some help for assignments in the NMR spectra of other borazaro heterocycles.

CONCLUSIONS

In spite of shortcomings in several instances, the agreement of predicted with observed electronic spectra is good for compounds with only two heteroatoms. Predictions made in Tables I, II, and IV – VIII for energies and intensities in spectra of such compounds are probably quite reliable. As the ratio of heteroatoms to carbon atoms increases, the reliability undoubtedly decreases but it is hard to say exactly how much, until more compounds of this type have been studied experimentally. For the extreme case of borazine only an order-of-magnitude agreement is obtained, predicted energies being much too low; the same is likely to happen for the naphthalene analogue of borazine although the order of state symmetries and relative transition intensities are probably predicted correctly.

In borazaro analogues of alternant hydrocarbons, transition energies are rarely shifted appreciably with respect to the parent hydrocarbons. This should no longer be the case for analogues of non-alternant hydrocarbons, of which none are known so far. Such a difference is in line with a simple application of the perturbation theory to the parent hydrocarbons using a model in which B^- and N^+ each contribute one electron to the π system and are considerably less and considerably more electro-negative than carbon, respectively.

Results for ionization potentials appear quite good but few experimental data are available for comparison. This also applies to calculated electron distributions. The perfect correlation with reported ^{11}B NMR shifts is quite astonishing and additional experimental data will be awaited eagerly.

Parts of this work were done during the association of the author with the Institute of Physical Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia, and Kemisk Institut, Aarhus University, Aarhus, Denmark. The author is grateful to Dr J. Janata, Petrochemical and Polymer Laboratory, ICI Ltd., Runcorn, Cheshire, England, for a communication of unpublished results on the polarographic behavior of compounds I–VI. Completion of the work was assisted by NSF Grant No GP-11170.

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