5 g. (67%) of XIX, m.p. 245–247°, $[\alpha]_{\text{D}}$ +392°, $\lambda^{\text{EtOH}}_{\max}$ 240 mμ (16,730); λ^{KBr} 2.94 (-OH), 5.58, 6.07, 6.24, 6.32 μ.

Anal. Calcd. for $C_{22}H_{28}O_3N_2$ (368.4): C, 71.71; H, 7.66; N, 7.60. Found: C, 71.55; H, 7.88; N, 7.35.

16α,17α,21-[3,1,1-(2-Pyrazolino)]-4-pregnen-3,11,20-trione (XX).—A solution of 2 g. of 16α,17α,21-[3,1,1-(2-pyrazolino]-4-pregnen-11α-ol-3,20-dione in 30 ml. of glacial acetic acid was cooled in ice and mixed with a cold solution of 750 mg. of chromic anhydride in 5 ml. of water and 15 ml. of acetic acid. The mixture was kept at 0° for 10 min. and then at 25° for 3 hours. The solution was poured into 500 ml. of water, 500 ml. of ethyl acetate was added and the aqueous layer was made slightly alkaline by adding a strong solution of sodium hydroxide while cooling with ice. The ethyl acetate layer was separated and the water layer was again extracted with ether–ethyl acetate 1:1. The combined organic extracts were washed with water, dried over magnesium sulfate and evaporated. The residue was crystallized from methylene chloride–ether to yield 1.3 g. (65%) of XX, m.p. 229–230°. After passage over a column of alumina, crystallization from ether gave prisms, m.p. 230–233°, $[\alpha]_{\text{D}}$ +440°, $\lambda^{\text{MEOH}}_{\max}$ 237 mμ (17,000); λ^{KBr} 5.60, 5.86, 6.0, 6.16, 6.31 μ.

Anal. Calcd. for $C_{22}H_{26}O_3N_2$ (366.4): C, 72.10; H, 7.15; N, 7.65. Found: C, 71.80; H, 7.13; N, 7.77.

16α,17α,21-[(3,1,1-(2-Pyrazolino)]-4-pregnen-11β-ol-3,20-dione (XXIII).—A 5% by volume aqueous spore suspension of *Cunninghamella* sp. M 2047 was used to inoculate three 100-ml. portions of medium as described above for XIX, and the medium was incubated for 72 hours at 27° on a rotary shaker at 240 r.p.m. Eight 600-ml. portions of this same medium were each inoculated with 3% by volume of the vegetative culture and were incubated for 48 hours. To each of the flasks was added 300 mg. of XVI dissolved in 7.5 ml. of acetone and incubation was continued on the shaker for an additional 24 hours. The whole culture was extracted 3 times with 0.5 volumes of methylene chloride and the combined extracts were concentrated under reduced pressure to dryness. The residue was chromatographed over a column of 30 g. of alumina. Fractions 16 through 18 (ether–methylene chloride 3:2) were collected and recrystallized from ether–methylene chloride to give 140 mg. (6%) of XXIII, m.p. 255–258°, $[\alpha]_{\text{D}}$ +450°, $\lambda^{\text{EtOH}}_{\max}$ 240 mμ (17,600); λ^{KBr} 2.94, 5.58, 6.00, 6.20, 6.29 μ.

Anal. Calcd. for $C_{22}H_{28}O_3N_2$(368.4): C, 71.71; H, 7.66; N, 7.60. Found: C, 71.61; H, 7.40; N, 7.92.

In the preparation of XXIII from XX, 500 mg. of the triketone was dissolved in a mixture of 750 mg. of pyridine, 5 ml. of water and 30 ml. of methanol containing 1.0 g. of semicarbazide hydrochloride. The solution was refluxed for 18 hours, and then evaporated to one-half volume and slowly diluted with water. The white precipitate was filtered, washed and dried to give 620 mg. of semicarbazone, m.p. < 200°. Without purification this material was dissolved in 18 ml. of tetrahydrofuran and 9 ml. of water and treated with 400 mg. of potassium borohydride. The solution was refluxed for 7 hr. during which an additional 100 mg. of hydride was added. After acidification with acetic acid the solution was concentrated, diluted with water and the precipitate collected; 500 mg. This product was hydrolyzed by refluxing for 6 hr. with a mixture of 7.5 ml. of acetic acid, 2.5 ml. of water, 1.5 ml. of pyruvic acid and 5 ml. of tetrahydrofuran. The solution was evaporated to dryness at 60° and the residue was washed with water and dried, giving 200 mg. of pale tan powder. Chromatography on 4 g. of alumina in methylene chloride–ether gave 10 mg. of colorless crystals of XXIII, m.p. 245–247°, infrared spectrum identical with material obtained from microbiological oxidation.

3-Ethylenedioxy-16α,17α,21-[3,1,1-(2-Pyrazolino)]-5-pregnene-11,20-dione (XXI).—A solution of 500 mg. of XX in 10 ml. of ethylene glycol, 65 ml. of benzene and 50 mg. of *p*-toluenesulfonic acid was heated for 6 hr. under a reflux condenser fitted with a tube for water removal. The solution was cooled, made alkaline with 20% sodium hydroxide solution and extracted with 50 ml. of methylene chloride and 50 ml. of ether. The organic layer was washed with water, dried, evaporated to dryness *in vacuo* and the residue was chromatographed over 10 g. of alumina using ether and methylene chloride. The crystalline fractions were combined and crystallized from ether to yield 250 mg. (45%) of XXI, m.p. 238–240°, $[\alpha]_{\text{D}}$ + 202°; λ^{KBr} 5.59, 5.87, 5.89 (weak, Δ^5), 6.30.

Anal. Calcd. for $C_{24}H_{30}O_4N_2$ (410.5): C, 70.22; H, 7.37; N, 6.82. Found: C, 70.32; H, 7.41; N, 6.67.

3-Ethylenedioxy-16α,17α,21-[3,1,1-(2-pyrazolino)]-5-pregnen-20β,ol-11-one (XXII).—To a solution of 100 mg. of XIX dissolved in 50 ml. of methanol was added a solution of 100 mg. of sodium borohydride in 3 ml. of water. An additional 10 ml. of methanol was added and the solution was warmed to 50° until all the solid had dissolved and then was allowed to stand at 25° for 7 hr. After concentrating on the steam-bath the solution was diluted with water and the crystalline precipitate was collected, washed with water and dried, giving 70 mg. (70%) of colorless fine needles, m.p. 305–310° dec., $[\alpha]_{\text{D}}$ + 195°; λ^{KBr} 3.05, 5.86, 6.29 μ.

Anal. Calcd. for $C_{24}H_{32}O_4N_2$ (412.5): C, 69.87; H, 7.82; N, 6.79. Found: C, 69.68; H, 7.75; N, 6.69.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

π-Complexes. II.[1] Charge Transfer Spectra of π-Complexes Formed by Tetracyanoethylene with Polycyclic Aromatic Hydrocarbons and with Heteroaromatic Boron Compounds[2]

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The charge transfer spectra of the π-complexes formed by tetracyanoethylene with a number of polycyclic aromatic hydrocarbons and with various heteroaromatic compounds of boron have been measured in chloroform solution. The results for the hydrocarbons were consistent with the molecular orbital treatment given in Part I.[1] The results for the boron compounds lead to estimates of the molecular orbital parameters for boron.

In the first paper[1] of this series a simple molecular orbital treatment was given of the charge transfer spectra of the complexes formed between aromatic compounds and acceptors such as trinitrobenzene, picric acid or chloranil. Complexes of this kind are treated as weak π-complexes formed by mutual interaction of the π-orbitals of the donor (A) and acceptor (B). Since the interaction is weak it should lead to only relatively minor changes in the energies of the individual orbitals; the absorption bands of A and B should consequently appear almost unchanged in the spectrum of the complex. However there is the additional possibility in the complex of charge transfer transitions in which an electron initially occupying an orbital i of A jumps into one of the empty orbitals j of *B*. The transition energy ΔE_{ij} for this process should be given by

$$\Delta E_{ij} = B_j - A_i \tag{1}$$

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[1] Part I, *J. Am. Chem. Soc.*, **84**, in press (1962).

[2] This work was supported by a grant from the National Science Foundation.

where A_i, B_j are the energies of the orbitals i, j, respectively. If the donor is a polycyclic aromatic hydrocarbon the energies of its orbitals are given in simple molecular orbital theory by

$$A_i = \alpha + \beta x_i \tag{2}$$

where α is the coulomb integral of carbon and β the carbon-carbon resonance integral, x_i being a number calculated theoretically. The transition energies of the first charge transfer bands for the complexes formed by such hydrocarbons with a given donor should then be of the form

$$\begin{aligned} \Delta E_{ij} &= (B_j - \alpha) - \beta x_i \\ &= \text{constant} - \beta x_i \end{aligned} \tag{3}$$

since B_j will be constant, being the energy of the lowest unoccupied orbital of the acceptor. Hence ΔE_{ij} should be a linear function of the theoretical quantity x_i, regardless of the values of the parameters α, β and of B_j.

These relations were shown[1] to hold for the complexes formed by a number of polycyclic hydrocarbons with trinitrobenzene. The slope of the plot of ΔE_{ij} against x_i led to a reasonable value for β and the intercept to a reasonable value for the energy of the lowest unoccupied orbital of trinitrobenzene. The spectra of the complexes formed by several derivatives of 10,9-borazarophenanthrene with trinitrobenzene were also measured; these led to an estimate of the energy of the highest unoccupied orbital of the borazarophenanthrene and this in turn to an estimate of the resonance integral of the boron-nitrogen bond.

The purpose of the present investigation was to provide a further check of eq. 3 and to determine the remaining molecular orbital parameters for boron. The complexes with trinitrobenzene had proved unsuitable for this latter purpose for two reasons. First, the parent borazarophenanthrene was oxidized by trinitrobenzene and the spectrum of its complex could not therefore be measured; the energy of its highest occupied orbital could therefore be obtained only by an uncertain extrapolation from the spectra of the complexes formed by its derivatives. Secondly, the charge transfer bands of complexes formed by trinitrobenzene lie in the same region as the bands due to the normal π-π^* transitions of the donors and of trinitrobenzene itself; consequently it is often difficult to determine the frequencies of the charge transfer bands.

We encountered similar difficulties with the complexes formed by most of the other usual acceptors, *e.g.*, picric acid, iodine, chloranil, trinitrofluorenone and dichloromaleic anhydride. Eventually we found that the complexes formed by tetracyanoethylene are almost ideal for the present purpose. These absorb at very low frequencies, even the benzene complex being colored[3] and 10,9-borazarophenanthrene and 2,1-borazaronaphthalene both form stable complexes whose spectra can be measured without difficulty. Merrifield and Phillips[3] have reported measurements of such spectra for a number of complexes formed by tetracyanoethylene; however the only unsubstituted hydrocarbons studied by them were benzene, naphthalene, diphenyl, *m*- and *p*-terphenyl and pyrene. We have therefore measured the charge transfer spectra of a considerable number of complexes formed by tetracyanoethylene with polycyclic aromatic hydrocarbons and with a variety of heteroaromatic boron compounds whose synthesis has been described in a recent series of papers.[4]

Experimental

Materials.—Pyrene and naphthalene were purified by sublimation; the remaining hydrocarbons were used as supplied by the Aldrich Chemical Co. The m.p.'s agreed with the values reported in the literature. Tetracyanoethylene was also used as supplied without further purification. The borazarophenanthrenes were prepared by the methods previously described.[4] The borazaronaphthalenes and boroxarophenanthrenes were supplied by Dr. R. Dietz[4] and the anthracene and pyrene analogs by Mr. S. S. Chissick.[4] All these compounds were purified by recrystallization from petroleum ether or benzene- petroleum ether except the anthracene and pyrene analogs which were analytical specimens. The chloroform used for spectroscopic measurements was Eastman Kodak Co. spectral grade.

Spectroscopic Measurements.—Solutions of the complexes were prepared by mixing equal volumes of solutions of the donor and tetracyanoethylene (0.02 *M*) in chloroform. The donor solutions were 0.02 *M* except for one or two hydrocarbons which were less soluble and were therefore used as saturated solutions of known strength. The spectra were measured in 1-cm. cells in the range 340–900 mμ (340–1100 mμ in the case of perylene) on a Cary model 14 spectrophotometer. No attempt was made to determine the equilibrium constants for formation of the complexes or the extinction coefficients of the charge transfer bands since these were irrelevant to the present investigation.

Results

Table I lists the wave lengths and frequencies found for the first charge transfer bands of the twenty-one hydrocarbons studied and also the energies of their highest occupied orbitals as calculated by the Hückel method with neglect of overlap. These energies were taken from a recent compilation[5] except for the values marked with asterisks which were calculated by Dr. L. Snyder at Bell Telephone Laboratories. The values listed are the numbers x_i of eq. 2. Data from the literature[3] for biphenyl and *m*- and *p*-terphenyl are included.

The numbers x_i are plotted against the observed transition energies in Fig. 1; the points are seen to lie close to a straight line as eq. 3 requires. The line in Fig. 1 was fitted by the method of least squares.

Table II lists the wave lengths and frequencies of the first charge transfer bands for the heteroaromatic compounds considered.

Discussion

The points in Fig. 1 lie close to a straight line as eq. 3 requires; better agreement could not be expected in view of the crudity of the Hückel approximation. Equation 3 also requires that the slopes of the lines obtained from data for complexes with different acceptors should be the same, being equal to β; from the slope of the line in Fig. 1 one finds:

$$\beta = -3.06 \text{ e.v.} \tag{4}$$

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[3] *Cf.* R. E. Merrifield and W. D. Phillips, *J. Am. Chem. Soc.*, **80**, 2778 (1958).

[4] M. J. S. Dewar, R. Pettit and V. P. Kubba, *J. Chem. Soc.*, 3073 (1958); M. J. S. Dewar and R. Dietz, *ibid.*, 2728 (1959); 1344 (1960); M. J. S. Dewar, R. Dietz, V P. Kubba and A. R. Lepley, *J. Am. Chem. Soc.*, **83**, 1754 (1961); S. S. Chissick, M. J. S. Dewar and P. M. Maitlis, *Tetrahedron Letters*, No. **23**, 8 (1960).

[5] C. A. Coulson and R. Daudel, "Dictionary of Values of Molecular Constants."

TABLE I

CHARGE TRANSFER BANDS OF COMPLEXES FORMED BY POLYCYCLIC AROMATIC HYDROCARBONS WITH TETRACYANOETHYLENE AND THE HÜCKEL ENERGIES OF THE HIGHEST OCCUPIED MO'S OF THE HYDROCARBONS

Compound	Code number	Wave length of charge transfer band, mμ	Frequencies of charge transfer band (KK)	Energy of highest occupied MO ($x\beta^{-1}$)
Benzene	1	385 ± 2	26.0	1.000
Naphthalene	2	560 ± 5	17.8	0.618
Acenaphthylene	3	502 ± 5	19.9	.637
Azulene	4	740 ± 2	13.5	.477
1,2-Benzanthracene	5	748 ± 5	13.9	.452
1,12-Benzoperylene	6	812 ± 5	12.3	.439
3,4-Benzotetraphene*	7	800 ± 5	12.5	.405
1,2-Benzopyrene*	8	705 ± 2	14.2	.497
3,4-Benzopyrene*	9	820 ± 2	12.2	.371
Chrysene	10	630 ± 2	15.9	.520
Coronene	11	725 ± 5	13.8	.539
1,2,5,6-Dibenzanthracene	12	635 ± 2	15.7	.473
1,2,3,4-Dibenzanthracene	13	667 ± 5	15.0	.499
1,2,7,8-Dibenzanthracene	14	635 ± 2	15.7	.491
1,2,3,4-Dibenzopyrene*	15	730 ± 5	13.7	.398
1,2,4,5-Dibenzopyrene*	16	790 ± 5	12.7	.442
Perylene	17	920 ± 5	10.9	.347
Phenanthrene	18	540 ± 2	18.5	.605
Picene	19	590 ± 2	16.9	.501
Pyrene	20	720 ± 2	13.9	.445
Triphenylene	21	570 ± 2	17.5	.684
Biphenyl	22	500[3]	20.0	.704
m-Terphenyl	23	500[3]	20.0	.662
p-Terphenyl	24	564[3]	17.7	.592

TABLE II

CHARGE TRANSFER SPECTRA OF COMPLEXES FORMED BY VARIOUS HETEROAROMATIC BORON COMPOUNDS WITH TETRACYANOETHYLENE AND DERIVED VALUES FOR THE ENERGIES OF THEIR HIGHEST OCCUPIED MO'S

Compound	Wave length of charge transfer band, mμ	Frequency of charge transfer band $\times 10^{-3}$	Energy of highest occupied MO from Fig. 1 ($x\beta^{-1}$)
10,9-Borazarophenanthrene	633 ± 2	15.8	0.535
10-Methyl-10,9-borazarophenanthrene	605 ± 2	16.5	.56
10-Hydroxy-10,9-borazarophenanthrene	635 ± 2	15.7	.53
2,1-Borazaronaphthalene	475 ± 5	21.1	.75
2-Methyl-2,1-borazaronaphthalene	540 ± 2	18.5	.645
2-Phenyl-2,1-borazaronaphthalene	550 ± 5	18.3	.64
Bis-2,1-borazaro-2-naphthyl ether	558 ± 5	17.9	.62
2-Methyl-3-chloro-2,1-borazaronaphthalene	515 ± 2	19.4	.68
2-Methyl-3-bromo-2,1-borazaronaphthalene	505 ± 2	19.8	.70
10-Hydroxy-10,9-boroxarophenanthrene	550 ± 2	18.3	.64
6,8-Dibromo-10,hydroxy-10,9-boroxarophenanthrene	470 ± 2	21.3	.76
10-Phenyl-10,9-boroxarophenanthrene	520 ± 2	19.2	.67
2,7-Diphenyl-2,7-dibora-1,8-diazaroanthracene	665 ± 5	15.0	.50
1,2,7,8-Tetraphenyl-2,7-dibora-1,8-diazaroanthracene	665 ± 5	15.0	.50
2,6-Diphenyl-2,6-dibora-1,7-diazaropyrene	600 ± 5	16.7	.57

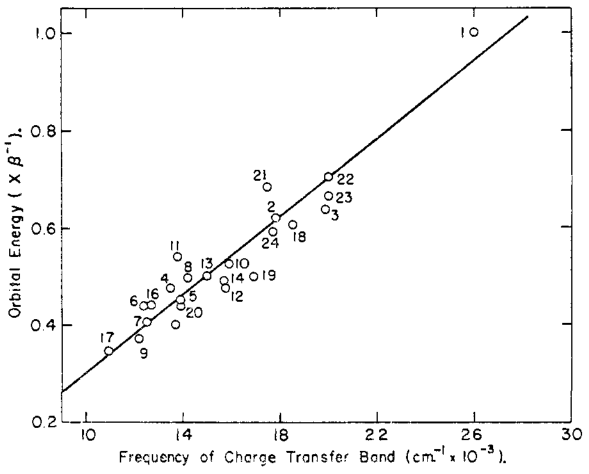

Fig. 1.—Plot of the transition energies of the charge transfer bands of hydrocarbon–tetracyanoethylene complexes against the energies of the highest occupied orbitals of the hydrocarbons; the points are numbered according to the code in Table I.

This agrees very well with the values found[1] from the corresponding trinitrobenzene complexes (3.0 e.v.) and from the spectrum of benzene (3.1 e.v.). The intercept of the line with the x-axis should give the energy of the lowest unoccupied orbital of tetracyanoethylene

$$B_j = -0.11\beta \qquad (5)$$

This seems a reasonable value.

Thus the simple MO treatment seems once more to give a very satisfactory account of the charge transfer spectra of hydrocarbon complexes and so by inference to support our underlying assumptions concerning their structure. These compounds are best regarded as loose polarization complexes in which the components retain their electronic structures essentially unchanged. The term "charge transfer complex" seems to us misleading since it implies a significant change in the structures of the components.

The success of the simple MO treatment suggests that the energies of the highest occupied MO's of heteroaromatic compounds may be estimated from the transition energies of the charge transfer bands of their corresponding complexes. Comparison of the energies of the orbitals found in this way with those estimated by the Hückel treatment provides a novel method for estimating the molecular orbital parameters of heteroatoms.[1]

This approach has a number of advantages over the methods that have been used previously, in particular those based on comparisons of calculated and observed dipole moments, spectra and chemical reactivities. The use of dipole moments is invalidated by the difficulty of estimating the effects of hybridization. Thus the dipole moments of the bonds formed by sp^2 nitrogen must differ from those formed by nitrogen in its "normal" sp^3 state and the same must be true of pairs of unshared electrons occupying hybrid orbitals of nitrogen. It is impossible to estimate these differences theoretically in any convincing manner— and of course there are no suitable reference compounds with unconjugated nitrogen atoms in a planar sp^2 configuration. The use of spectra is unsatisfactory since the Hückel method cannot easily be applied to calculations of transition energies; this is because it gives an average of the first singlet–singlet and first singlet–triplet transition energies and the singlet–triplet transition energies are usually not known. This difficulty should not arise in the case of charge transfer spectra where the excited singlet and triplet states should be much closer together in energy. Finally the use of chemical reactivities suffers from uncertainty concerning the structures of transition states and complications due to solvent effects.

The straight line in Fig. 1 can then be used to estimate the energies of the highest occupied MO's of aromatic compounds in general from the transition energies of the charge transfer bands of the complexes formed by them with tetracyanoethylene. The values for the boron compounds studied here are listed in the last column of Table II. The energies of the orbitals are given in the form indicated in eq. 2, *i.e.* in units of β, the carbon–carbon resonance integral, relative to the energy (α) of a carbon 2p-AO.

The orbital energies in a heteroaromatic compound can be estimated from those for the corresponding isoaromatic hydrocarbon by the perturbation methods introduced by Coulson and Longuet-Higgins.[6] The energy A_i of the heteroaromatic orbital is given in terms of that (A_i) for the hydrocarbon by

$$A_i' = A_i + \sum_r a_{ir}^2(\alpha_r - \alpha_c) + \sum_{r,s} a_{ir}a_{is}(\beta_{rs} - \beta) \qquad (6)$$

where a_{ir} is the coefficient of the atomic orbital of atom r in the orbital of the hydrocarbon, α_r is the coulomb integral of atom r in the heteroaromatic compound and β_{rs} is the corresponding resonance integral between atoms r, s. In our case five parameters are needed

$$\alpha_B \quad \alpha_N \quad \beta_{CB} \quad \beta_{CN} \quad \beta_{BN} \qquad (7)$$

We may reasonably assume as a first approximation that the differences between boron and carbon, and between carbon and nitrogen, are similar; in that case

$$\alpha_B - \alpha_C = \alpha_C - \alpha_N \qquad (8)$$

and

$$\beta_{CB} = \beta_{CN} \qquad (9)$$

This leaves three independent quantities to be determined.

The data in Table II include values for unsubstituted 10,9-borazarophenanthrene and 2,1-borazaronaphthalene; the energies of their highest occupied orbitals can be estimated directly from those of phenanthrene and naphthalene by using eq. 6. No values are available for the other parent ring systems, in particular 2,6-dibora-1,7-diazaropyrene and 2,7-dibora-1,8-diazaroanthracene. However the data listed in Table II indicate that substituents of inductive or $\pm E$ type do not have a large effect on the orbital energies and this is supported by a comparison of the data for the diphenyl and tetraphenyl derivatives of the diboradiazaroanthracene. Here and in the corresponding pyrene derivative the phenyl groups must in any case be forced out of coplanarity with the central nucleus so that the resonance interactions between them are probably small. Table III lists energies of the highest occupied orbitals calculated on this basis; the values are again in units of β relative to the energy of a carbon $2p$-AO.

TABLE III

COMPARISON OF THE ENERGIES OF THE HIGHEST OCCUPIED MO'S OF FOUR BORON-CONTAINING HETEROAROMATIC COMPOUNDS DEDUCED FROM SPECTRAL DATA

Compound	Energy of highest occupied MO ($x\beta^{-1}$)
2,1-Borazaronaphthalene	0.75
10,9-Borazarophenanthrene	.535
2,7-Dibora-1,8-diazaroanthracene	.50
2,6-Dibora-1,7-diazaropyrene	.57

Comparison of these values with the ones calculated from eq. 6–9 enables us to estimate the molecular orbital parameters. The values found from the data for the first three compounds in Table III are

$$\alpha_B = \alpha_C - 1.59\beta;\ \alpha_N = \alpha_C + 1.59\beta \qquad (10)$$
$$\beta_{CB} = \beta_{CN} = 0.90\beta;\ \beta_{BN} = 0.50\beta$$

The value calculated for the energy of the highest occupied orbital of the diboradiazaropyrene, using these parameters, is 0.55β, in good agreement with the value listed in Table III.

The values in eq. 10 seem reasonable. The coulomb integral for nitrogen is similar to the values that have been found appropriate for other heteroaromatic compounds containing secondary nitrogen.[7] The resonance integrals also seem reasonable if one remembers that variations in bond order have been neglected in the simple perturbation treatment used here. Undoubtedly the bonds involving heteratoms will have lower orders than the corresponding bonds in the hydrocarbon; these differences will be absorbed into the empirical resonance integrals and so reduce their values. Equations 10 shows that, as expected, the decrease is greater the greater the difference in electronegativity between the bonded atoms.

The work described in this paper therefore seems to provide further justification for the simple MO treatment of molecular complexes and also for our new approach to the problem of determining MO parameters for heteroatoms. The values given here are provisional and may require revision when data for additional boron-containing ring systems become available; a number of such compounds are being synthesized here at the present time.

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(6) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (London), **A191**, 39 (1947); **A193**, 447, 456 (1948); **A195**, 188 (1948).

(7) *Cf.* R. D. Brown and M. L. Heffernan, *Trans. Faraday Soc.*, **54**, 757 (1958); *Austral. J. Chem.*, **12**, 319 (1959).