JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 90, NUMBER 7 MARCH 27, 1968

Physical and Inorganic Chemistry

Semiempirical SCF–MO Calculations, Employing Complete Valence Orbital Basis Sets, for Methyl-Substituted Borazines and Benzenes[1]

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Abstract: Molecular orbital calculations were carried out under approximations which minimize the introduction of adjustable parameters. One set involved the assumption of localized σ bonds and lack of σ–π exchange. This method was attractive from the computational standpoint and as a test of qualitative bonding arguments, but the results are in poor agreement with experimental ionization potentials. The second set involved the use of Pople and Segal's CNDO method. Calculated ionization potentials are in reasonable agreement with experiment for the methyl-substituted benzenes. Results for the borazines are less satisfactory, since in some cases the highest filled orbital is calculated to have σ symmetry, which appears to be in conflict with observed trends in ionization potentials and electronic spectra. (This same incorrect ordering is evident in published extended Hückel calculations.) If σ-type orbitals are ignored, CNDO calculations reproduce trends in the ionization potentials and electronic spectra for borazine and methylborazines. The parameter choice in Hückel and Pariser–Parr–Pople-type calculations for B–N systems is discussed in light of the CNDO results.

The borazine molecules include atoms of significantly different electronegativity and thus provide an interesting contrast with the isoelectronic hydrocarbons, for which extensive experimental and theoretical data are available. Previous theoretical calculations on borazine include simple and extended Hückel-type calculations[3–5] and Pariser–Parr–Pople-type SCF calculations.[6,7] In addition, the influence of phenyl substituents on the reduction potentials and charge-transfer spectra of borazines has been correlated within the framework of Huckel theory,[8,9] and methyl- and chloro-substituent effects have been discussed within the framework of Pariser–Parr–Pople and Huckel treatments.[10–12]

Except for the work of Hoffmann,[5] all of the foregoing studies have necessitated either empirical or arbitrary choice of parameters which account for the polarity of the σ framework. Furthermore, the work of Davies[7] and of Chalvet, Daudel, and Kaufman[6] has made it clear that the π calculations are sensitive to the model chosen to represent the σ framework. We were prompted to undertake the calculations reported here when it became clear that reasonable parameter choices would allow one to fit the ionization potentials of methyl-substituted borazines in the Hückel approxi-

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(1) Abstracted from the Ph.D. Thesis of P. M. Kuznesof, Northwestern University, 1967.

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mation by either inductive or hyperconjugative models.[13]

In an attempt to eliminate the need for arbitrary fixed choices of core charges and for parametric representation of substituent groups, we have employed a method which includes a simplified SCF calculation on the σ system, along with a Pariser–Parr–Pople-type of SCF calculation on the π system. Interaction between the σ and π systems is introduced only through the diagonal matrix element of the SCF Hamiltonian; thus, the calculation is close in form to the usual Pariser–Parr–Pople π-only calculations, but does not involve the arbitrary description of the σ framework. Calculations along a similar line have been performed by Parks and Parr[14] in their study of the electronic structure of formaldehyde, by Cahill and Miller[15] on the acetaldehyde molecule, and by McEwen[16] on N–O compounds.

At the next level of approximation, calculations were performed with the CNDO method which has been developed recently by Pople and coworkers.[17–19] Pople's group has demonstrated impressive agreement between calculated and observed dipole moments, structures, and force constants of a large number of simple molecules.[18,19] The present work provides a test of the CNDO method in the calculation of electronic spectra and ionization potentials for large heteronuclear molecules.[20]

Calculations

Inductive Model. In this model the σ framework is approximated by a collection of two-center localized SCF molecular orbitals formed from appropriate hybrid or atomic orbitals, and the π system is treated by conventional Pople theory. By invoking the zero differential overlap approximation[21–23] and ignoring two-electron exchange integrals between p_π and σ atomic orbitals, the matrix elements for the SCF Hamiltonian are

$$F_{\mu\mu} = U_{\mu\mu} + (Q_I - {}^1\!/_2 q_{\mu\mu} + P_I)\gamma_{II} + \sum_{J(\neq I)} (P_J + Q_J - \zeta_J)\gamma_{IJ} \qquad (1)$$

$$F_{\mu\nu} = \beta_{\mu\nu} - {}^1\!/_2 q_{\mu\nu}\gamma_{IJ} \quad (\mu \neq \nu) \qquad (2)$$

where the μth atomic orbital belongs to atom I and the νth to atom J. Q_I is the total σ electron density on atom I, P_I is the π electron density, and q's are charge-density bond-order terms,[22] for either the σ or the π molecular orbitals. The two-center, two-electron repulsion term, γ_J, is discussed below and ζ_J is the net core charge (*i.e.*, nucleus plus $1s^2$ for second period atoms).

An initial $F(\pi)$ matrix generated from Huckel coefficients is used for a starting set of π bond orders and charge densities. Assuming neutral atom electron densities, the initial $F(\sigma)$ matrix is constructed and energies, wave functions, charge densities, and bond orders are calculated for the σ system. The calculation is then alternated between the σ and π systems until the desired degree of self-consistency in the coefficients is attained. Since all off-diagonal F elements between σ and p_π atomic orbitals are zero, changes in the charge distribution of the σ system will be manifested in the π system only through the Q_I term in eq 1. Hence, the model is called the *inductive* model.

Conjugative Model. The CNDO/1 approximation of Pople, Segal, and Santry is used here.[17–19] The F matrix elements take the form of eq 1 and 2 with μ and ν indexing all valence orbitals. The sum $Q_I + P_I$ is now replaced by C_I, the total electron-density on atom I, and the charge bond-order matrix elements, $q_{\mu\nu}$, are calculated from atomic orbital coefficients in all occupied molecular orbitals.

Electronic Properties. The ionization potential of a molecule is the energy difference between the ground-state molecule and the molecular ion. Then strictly, it is necessary to solve the open-shell problem[24] for the ion as well as the closed-shell problem for the neutral. Open-shell formulations for the "π-only" SCF method and CNDO method have been developed,[19,25] and the inductive model was adapted easily for these calculations according to Bristock and Pople's procedure.[25]

Wave functions for the excited states were obtained by including limited configuration interaction between molecular orbitals calculated for the ground state, and the corresponding excitation energies were calculated from the formulas of Roothaan.[26] Elements of the configuration interaction matrix have been given elsewhere.[27] These were expanded over atomic orbitals and evaluated in the framework of the zero differential overlap approximation.

Evaluation of Integrals and Parameters. Slater obitals were used for evaluating overlap integrals from the formulas of Mulliken, *et al.*[28,29] The Slater Z values for H, B, C, N, O, and F are 1.2, 2.6, 3.25, 3.9, 4.55, and 5.2.

The core matrix elements for the one-electron Hamiltonian, $U_{\mu\mu}$, given in Table I, are evaluated from the equation

$$U_{\mu\mu} = W_\mu - (\zeta_I - 1)\gamma_{II}$$

analogous to one derived by Pople and Segal.[18] Va-

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[19] J. A. Pople and G. A. Segal, *ibid.*, 44, 3289 (1966). A similar method by G. Klopman, *J. Am. Chem. Soc.*, 87, 3300 (1965), and earlier papers, has been successful on simple molecules.

[20] A modification of the CNDO method, in which terms of the type $F_{\mu\nu}$ on the same center are omitted, has proved quite successful in the calculation of electronic structures of some linear molecules, CO, CN$^-$, CNH, and HCN: D. F. Shriver and J. Posner, *ibid.*, 88, 1672 (1966). While this modification appears to yield very good values for the orbital energies, it is not appropriate for the present calculations on large and asymmetrical molecules where it is essential for the calculation to be invariant to the rotation of the basis orbitals. After this paper was submitted, H. W. Kroto and D. P. Santry, *J. Chem. Phys.*, 47, 792 (1967), reported CNDO calculations of the electronic spectra for some small molecules.

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[29] Corrections to some original overlap integral formulas (R. S. Mulliken as noted in C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, Inc., New York, 1964, p 269) are taken into account.

Table I. Core Hamiltonian Matrix Elements (ev)[a]

Atom	Valence state	U_{ss}	U_{pp}
H	s	13.60	
B	spp	32.03	25.54
C	sppp	53.11	43.37
N	sp^2pp	78.32	65.82
		$U_{\sigma\sigma}$	$U_{\pi\pi}$
B	trtrπ	24.79	22.15
C	trtrtrπ	49.01	44.55
C	tetetete	54.42	
N	tr^2trtrπ	69.96	63.48

[a] U_{ss} and U_{pp} were used for conjugative calculations, and $U_{\sigma\sigma}$ and $U_{\pi\pi}$ for the inductive model.

lence-state ionization potentials, W_μ, of Hinze and Jaffé[30] were employed. For hydrogen $U_{\mu\mu} = W_{\mu\mu}$ was employed.

The resonance integral is expressed as[18]

$$\beta_{\mu\nu} = \frac{S_{\mu\nu}}{2}(\beta_I^0 + \beta_J^0)$$

where β_I^0 and β_J^0 are atom parameters to be evaluated empirically. It is, of course, desirable to obtain a set of β_I^0 which is transferable from molecule to molecule. Pople and Segal[18] have determined a set of β_I^0 by fitting their results on diatomic molecules to those obtained from *ab initio* SCF-LCAO calculations. Their set, here referred to as set b, employs $-\beta_I^0 = 9$, 17, 21, and 25 ev for H, B, C, and N, respectively. These values have been tested and compared with results from β_I^0 set a (first used by Pople in some early unpublished work), where $-\beta_I^0 = 9$, 13, 15, and 17 ev, in order to decide upon values which best reproduce the experimental data for some small molecules.

For the inductive model, the one-center, two-electron integrals, the γ_{II}'s, were evaluated by Pariser's method[31] while Paoloni's treatment[32] ($\gamma_{II} = 3.29Z$) was used for conjugative model calculations for second-row atoms. For hydrogen, $\gamma_{II} = 8.00Z$[33] was employed with both models. The orbital energies and charge densities for CO, H_2O, and HCN compared well with CNDO/1 results[18] which were obtained using theoretical values for the γ_{II} and γ_{IJ}.[34] Two-center, two-electron repulsion integrals were calculated using the Mataga-Nishimoto approximation.[27] Bond distances and angles were taken from or estimated from published data,[35] and for complex molecules, Cartesian coordinates were calculated by the use of program PRθXYZ.[36] Inductive model calculations were iterated until σ charge densities were reproduced to within 0.0003 and the orbital energies to within 0.03 ev. Unless otherwise noted, conjugative model calculations were iterated until the net atomic charge densities were self-consistent to 0.005 or better.

Results and Discussion

Ionization Potentials. Following the proposal of Koopmans and others, it is common practice to equate the vertical ionization potential with the negative of the corresponding orbital energy.[26,37] However, Koopmans' theorem ionization potentials for π-only SCF-MO calculations often are several electron volts higher than experimental values. Hoyland and Goodman[38] attribute this "ionization potential catastrophe" primarily to changes in the energy of the σ framework upon ionization. Therefore, an open-shell calculation on the ionized molecule (inductive model) was performed with the hope of minimizing this ionization potential catastrophe and predicting the correct ordering of the borazine ionization potentials. However, the results were anomalous; for example, results for ethylene and propylene gave ionization potentials of 26 and 47 ev, respectively. Therefore, in the remainder of this paper, Koopmans' theorem is employed. In these comparisons the trends and energy intervals due to substitution are more important than absolute energies.

The results for the inductive model show a poor correlation with experiment (Table II). For methyl-substituted ethylenes and methyl-substituted benzenes, the order of the highest filled molecular orbital (HFMO)

Table II. Comparison of Highest Filled Orbital Energies Obtained from SCF Inductive and Conjugative Model Calculations on Some Methyl-Substituted Hydrocarbons and Boron–Nitrogen Compounds

Molecule	Ionization potential, ev	Ref	Inductive,[a] ev	Conjugative,[a] ev β_I^0 set a	β_I^0 set b
C_2H_4	10.51	*d*	11.62	12.840	14.421
CH_3CHCH_2	9.73	*e*	11.42	11.723	12.694
trans-$CH_3(CH)_2CH_3$	9.13	*f*	11.36	11.121	11.822
$(CH_3)_2(CH)_2CH_3$	8.68	*g*	11.16	...	...
$(CH_3)_2(CH)_2(CH_3)_2$	8.30	*g*	10.98	...	...
C_6H_6	9.24	*e*	10.94	11.618	12.611
$CH_3C_6H_5$	8.82	*e*	...	11.081	11.973
1,3,5-$(CH_3)_3C_6H_3$	8.39	*e*	10.54	10.954	11.765
$(CH_3)_6C_6$	7.85	*g*	10.13	...	...
BH_2NH_2	...	...	...	13.709	...
$BHCH_3NH_2$	...	...	...	12.753	...
BH_2NHCH_3	...	...	...	12.483	...
BH_3NH_3	...	...	...	13.715	14.461
$BH_3NH_2CH_3$	...	....	...	13.427	14.167
$BH_3NH(CH_3)_2$	...	...	...	13.351	14.127
$BH_3N(CH_3)_3$	...	...	...	13.317	14.127
$(HBNH)_3$	9.77	*h*	11.00	11.975	...
$(CH_3)BNH)_3$	9.30	*h*	10.37	11.035[b]	...
$(HBNCH_3)_3$	9.07	*h*	10.97	11.354[c]	...
$(CH_3BNCH_3)_3$	8.77	*h*	10.33	...	...

[a] The minus sign is omitted. A Slater exponent of 1.0 for hydrogen and β_I^0 set a were used for the inductive model calculations. [b] Net charge densities were self-consistent to at least 0.004 after five rounds of iteration. [c] Net charge densities were self-consistent to at least 0.003 after five rounds of iteration. [d] W. C. Price and W. T. Tutte, *Proc. Roy. Soc.* (London), **A174**, 207 (1940). [e] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957). [f] K. Watanabe, private communication to J. Collins, and F. P. Lossing, *J. Am. Chem. Soc.*, **81**, 2064 (1959). [g] R. Bralsford, P. V. Harris, and W. C. Price, *Proc. Roy. Soc.* (London), **A258**, 459 (1960). [h] Reference 13.

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(32) L. Paoloni, *Nuovo Cimento*, **4**, 410 (1956).

(33) R. D. Brown, *Mol. Phys.*, 1, 304 (1958).

(34) We use $U_{\mu\mu} = 13.60$ ev for the hydrogen 1s orbital *vs.* 13.06 ev in ref 18, and $\zeta_I\gamma_{IJ}$ instead of V_{IJ} for the electron-core interaction.

(35) "Tables of Interatomic Distances," L. E. Sutton Ed., Special Publication No. 11, The Chemical Society, London, 1958; and No. 18, Supplement, 1965. A complete tabulation of the molecular geometries which were used is given in ref 1.

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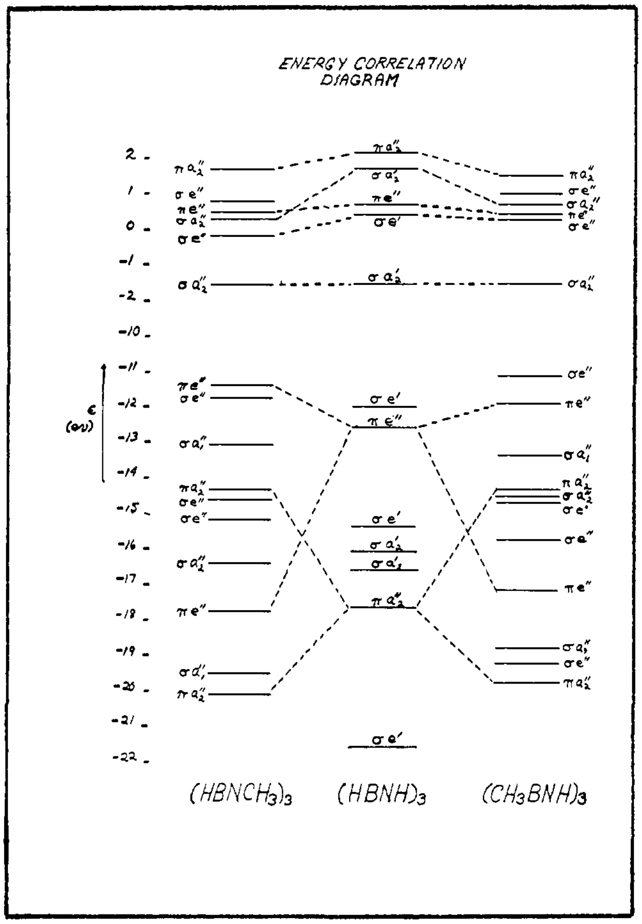

Figure 1. Energy correlation diagram for the methylborazines. These are results from SCF conjugative model (β_I^0 set a) calculations. The five lowest filled and ten highest vacant orbitals for the methylborazines are not shown. Also, the four lowest filled and five highest vacant orbitals for borazine are not shown. To aid in comparison, the symmetry labels for the D_{3h} point group are used. For a comment on the significance of the terms σ and π, see footnote 40.

energies parallels the ionization potentials; however, the intervals are much greater for experimental ionization potentials than for the calculated orbital energies. The agreement is even less satisfactory for the borazines where ionization potentials fall in the order $(HBNH)_3 > (CH_3BNH)_3 > (HBNCH_3)_3 > (CH_3BNCH)_3$, while the highest filled orbital energies fall in the order $(HBNH)_3 > (HBNCH_3)_3 > (CH_3BNH)_3 > (CH_3BNCH_3)_3$. Furthermore, it was found that variation of β_I^0 and γ_{IJ} values did not lead to an over-all improvement. Therefore, this inductive model is not appropriate for the representation of methyl-substituent effects on the borazines.

The conjugative model calculations more accurately reproduce the observed trends in ionization potentials. The results for hydrocarbons, presented in Table II, give satisfactory differences between the various methyl-substituted ethylenes and between the methyl-substituted benzenes. On the whole, β_I^0 set a appears to be the most satisfactory of the two.[39]

For both borazine and B-trimethylborazine the HFMO's are σ-type orbitals, whereas for N-trimethylborazine the HFMO is predominantly π in character.[40] Hoffmann has previously calculated that the highest filled MO of borazine has σ symmetry; however, a comparison of experimentally determined ionization potentials[13] with the present calculations indicates that a filled π level should be highest in energy for all the borazines. This inference is drawn from the observation that the HFMO's for the borazines fail to parallel the trends in ionization potentials; however, the highest filled π orbital energies do: 12.48, 11.88, and 11.35 ev for borazine, B-trimethylborazine, and N-trimethylborazine, respectively. An energy correlation diagram is given in Figure 1 for the highest filled and lowest vacant MO's of the borazines as calculated. The dashed lines connecting the filled $\pi(e'')$ MO's correctly show that methyl substitution on the nitrogen atom decreases the ionization potential of borazine more than does methyl substitution on boron.

Electronic Spectra. The MO diagram for borazine, Figure 1, in which the highest filled and lowest empty orbitals have σ symmetry would lead one to assign the spectrum to one-electron transitions $\sigma(e') \rightarrow \sigma^*(a_2')$ and $\sigma(e') \rightarrow \sigma^*(e')$. The former gives rise to $^{1,3}E'$ states, and the latter to singlet and triplet states of A_1', A_2', and E' symmetry. The calculated singlet energies (electron volts) are (5.97, 6.07),[41] E'; 7.74 A_2'; (8.28, 8.36),[41] E'; and 8.82 A_2'. However, an interpretation of the ultraviolet spectrum in terms of the $\sigma \rightarrow \sigma^*$ transition to two allowed E' states appears unsatisfactory. Only two bands actually are observed in the borazine spectrum, the $^1A_1' \rightarrow {}^1A_2'$ (partially allowed by vibronic coupling) and the $^1A_1' \rightarrow {}^1E'$; the band resulting from the $^1A_1' \rightarrow {}^1A_1'$ excitation presumably is buried between the other two (Table III).[42]

Table III. The Electronic Spectra of Borazine and Methylborazines[a]

	(HBNH)$_3$		(CH$_3$BNH)$_3$[b]		(HBNCH$_3$)$_3$[b]	
Symmetry	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
$^1A_2'$	8.48	6.5	8.06	6.5	7.50	5.5
$^3A_2'$	8.48		8.06		7.50	
$^1A_1'$	9.65	6.7	8.91	6.7	8.37	5.7
$^3A_1'$	7.96		7.81		7.20	
$^1E'$	9.86	7.2	8.95	7.0	8.58	6.5
$^3E'$	8.27		7.93		7.35	

[a] Energies are in ev. Observed spectra are from C. W. Rector, G. W. Schaeffer, and J. R. Platt, *J. Chem. Phys.*, **17**, 460 (1949). Calculated values are for $\pi \rightarrow \pi^*$ transitions (β_I set a). [b] For comparison with the borazine spectrum, the notation used here assumes D_{3h} symmetry, although C_{3v} notation is more appropriate. A transition to the excited $^1A_1$ state is allowed for a molecule of C_{3v} symmetry.

It seems unreasonable to assign the 6.5-ev band to a low-energy $^1A_1' \rightarrow {}^1E'$ transition because of the low

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[39] A comparison follows of our calculated orbital energies for benzene with calculated values of M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2367 (1966), and experimental ionization potentials, M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, 4434 (1964): 11.62 (π), 8.33 (π), 9.25; 11.73 (σ), 12.10 (σ), 11.49; 15.53 (σ), 15.27 (σ), *ca.* 12.19; 16.47 (σ), 15.48 (σ), 13.67; ..., ..., *ca.* 14.44; 17.54 (σ), 15.58 (π), 16.73; 17.99 (π), 15.79 (σ), 18.75; 23.51 (σ), 21.02 (σ), *ca.* 19.82 ev. M. F. El Sayed, M. Kasha, and Y. Tanaka, *J. Chem. Phys.*, **34**, 334 (1964), believe that the two lowest energy ionization processes lead to π states; however, as noted by Newton, *et al.*, this interpretation is equivocal.

[40] While σ–π orthogonality is lost in the methyl-substituted borazines and benzenes, orbitals of predominantly σ or π character are easily identified.

[41] The energy differences here are ascribed to the termination of the iteration in the CNDO calculation before a high degree of self-consistency in the coefficients had been attained.

[42] L. E. Jacobs, J. R. Platt, and G. W. Schaeffer, *J. Chem. Phys.*, 16, 116 (1948).

intensity of the band (log ϵ <3) compared with the 7.2-ev band (log ϵ >4).[43] Furthermore, the observed vibrational structure[43] would remain unexplained.

The lowest energy $\pi \rightarrow \pi^*$ single excitations for borazine are expected to give rise to three singlet and three triplet electronic states of symmetry A_1', A_2', and E' for which only transition to the E' state is allowed. The calculated and experimental excitation energies relative to the ground state are listed in Table III. Although the ordering of the excited states is correct, $^1A_2' < {}^1A_1 < {}^1E'$, the energy correlations are poor. The spectra of N-trimethylborazine and B-trimethylborazine were also calculated considering the lowest energy "π" $\rightarrow$ "π^*" transitions (Figure 1). The calculated energies are ordered correctly but are several electron volts above the observed values. The calculated effect, that N-methyl substitution causes a greater bathochromic shifts than does B-methyl substitution, is in agreement with the observed spectral shifts.

As a test on the adequacy of the above treatment, the spectrum of benzene (D_{6h} symmetry) also was calculated. Although the lowest vacant MO for benzene is calculated to be a $\sigma^*(b_{1u})$ orbital, a transition from the HFMO, $\pi(e_{1g})$ to $\sigma^*(b_{1u})$ gives rise to a symmetry-forbidden E_{2u} state. Configuration interaction was included for only the $\pi(e_{1g}) \rightarrow \pi^*(e_{2u})$ excitations. The results (observed values in parentheses) are as follows (ev): 5.36 (3.64),[44] $^3B_{1u}$; 6.20 (4.53),[45] E_{2u}; 7.05 (. . .), $^3B_{2u}$; 7.05 (4.71),[46] $^1B_{2u}$; 8.25 (5.96),[46] $^1B_{1u}$; 9.08 (6.76),[46] $^1E_{1u}$. The agreement with experiment is excellent if the *intervals* between the states are compared. The numerical results also compare very well with, for example, the π-only semiempirical calculations of Pariser and Parr,[21] and with the purely theoretical classic calculations of Goeppert-Mayer and Sklar.[47]

Judging from electronic spectra and ionization potentials, the CNDO method gives unreasonable ordering for the σ and π MO's in borazine.[48] However, satisfactory prediction of electronic properties of π electron systems is obtained if only the π MO's are considered; by contrast the inductive model does not appear successful. This comparison indicates, but certainly does not prove, that hyperconjugation is important in determining the properties discussed here.[49]

Charge Distribution and Diagonal Terms in the SCF Hamiltonian. In addition to the foregoing experimental checks on calculated energies, it is of interest to inspect the calculated charge distributions of the borazines which are listed in Table IV. These results indicate the polarity $B^+–N^-$ which reflects the greater electronegativity of nitrogen. This charge distribution is in harmony with the chemistry of borazines where addition of a hydrogen halide to the system results in proton attachment to nitrogen and halide to boron,[50] but it disagrees with more classical views of the bonding in borazines.[51] Extended Hückel calculations by Hoffmann indicated the same direction for the B–N bond polarity with net charges roughly four times those calculated in the present work.[5] This difference can be attributed to the well-known tendency of Hückel-type calculations to overestimate polarity. The present calculations indicate that the charge density in the p–π atomic orbital of boron amounts to 0.48 electron, which compares favorably with the value of 0.45 determined from nqr spectra for laminar boron nitride by Silver and Bray.[52]

Table IV. Net Atomic Charges, p_π Electron Densities, and Bond Orders for the Borazines[a]

	Conjugative model		
	$(HBNH)_3$	$(CH_3BNH)_3$[b]	$(HBNCH_3)_3$[c]
Q(B)	0.322	0.310	0.322
Q(N)	−0.231	−0.269	−0.235
Q(H(B))	−0.160	. . .	−0.164
Q(H(N))	0.069	0.058	. . .
$Q(CH_3)$	. . .	−0.099	0.076
Q(C)	. . .	0.002	0.178
π(B)	0.476	0.513	0.488
π(N)	1.524	1.561	1.487
π(C)	. . .	0.890	0.931
P(B–N)	0.572	0.538	0.571
P(B–C)	. . .	0.280	. . .
P(N–C)	. . .	. . .	0.162

[a] Calculations are for $\beta_I{}^0$ set a. Q = net atomic charge; π = p_π electron density; P = p_π–p_π bond order. [b] See footnote *b*, Table II. [c] See footnote *c*, Table II

The polarity associated with the methyl substituent presents a more subtle problem. For the hydrocarbons the methyl group is calculated to be more electron withdrawing in the σ framework than hydrogen. In this regard, recent microwave dipole moment data[53] indicate that the methyl group withdraws electrons more effectively than hydrogen in saturated systems (*i.e.*, through the σ system). A similar situation is encountered with the borazines where the methyl group is calculated to be electron releasing through the π system (Table IV, π(C)), and electron withdrawing through the σ framework when attached to boron, but electron releasing when attached to nitrogen. For both models, the methyl group bears a net negative

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(44) S. Leach, private communication to L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., New York, N. Y., 1966, p 432.

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(47) M. Goeppert-Mayer and A. L. Sklar, *ibid.*, 6, 645 (1938), as corrected by C. C. J. Roothaan and R. G. Parr, *ibid.*, 17, 1001 (1948).

(48) It should be emphasized that extended Hückel calculations[5] also give incorrect ordering of borazine molecular orbitals. Since this work was completed, M. J. S. Dewar and G. Klopman, *J. Am. Chem. Soc.*, **89**, 3089 (1967), have reported a method for determining the off-diagonal elements for the one-electron Hamiltonian which leads to a more logical ordering of σ and π orbital energies for some hydrocarbons.

(49) The relative importance of inductive *vs.* conjugative methyl-substituent effects has been the topic of considerable debate and results depend on approximations used. For examples, see M. D. Newton and W. N. Lipscomb, *J. Am. Chem. Soc.*, **89**, 2461 (1967); J. A. Pople and M. Gordon, *ibid.*, **89**, 4253 (1967); R. L. Flurry and P. Lykos, *ibid.*, **85**, 1033 (1963); M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962; F. A. Gray, I. G. Ross, and J. Yates, *Australian J. Chem.*, 12, 347 (1959).

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(53) V. W. Laurie and J. S. Muenter, *J. Am. Chem. Soc.*, **88**, 2883 (1966).

charge when attached to boron; however, it is more positive relative to hydrogen in borazine.

In their early treatment of borazine Roothaan and Mulliken assumed that the Hückel Coulomb integral is proportional to the electronegativity of the atom.[3] This led them to conclude that for borazine, α_N was the same amount greater than α_C in benzene as α_B was less. The SCF diagonal $F_{p\pi p\pi}$ elements of the present work which are the analogs of the Hückel α's are found to approximate Roothaan and Mulliken's proposal.

From the net charges and π charge densities given in Table IV we may calculate the core charge seen by the π electron. In borazine the values are +0.798 for boron and +1.293 for nitrogen. These are closely (but not exactly) related to the core charges, ζ_ν, which are used to compute the diagonal elements for a Pariser–Parr–Pople-type of calculation ($\zeta_\nu = \zeta_J - Q_J$ of eq 1). The problems associated with the choice of the P-P-P core charge for borazines have been recognized in the past but never thoroughly resolved. Davies[7] showed that, for the calculation of electronic spectra, it is not necessary to assign the polarity of the core, since this cancels out when energy differences are computed. Unfortunately, his method cannot be extended to the calculation of ionization potentials and other interesting properties. A somewhat different approach was adopted by Chalvet, Daudel, and Kaufman,[6] who employed two different sets of core charges, which bracket those calculated here. Future Pariser–Parr–Pople calculations on borazine-like molecules might be improved by the use of +0.8 and +1.2 core charges for boron and nitrogen, respectively.[54]

Acknowledgment. The authors are grateful for the generous allotment of computer time by the Vogelback Computing Center of Northwestern University. We also wish to acknowledge a conversation with Professor J. A. Pople in which he described the CNDO method before published accounts were available.

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(54) Occasionally the core charge is identified as the number of electrons donated to the π system by an atom. This terminology is to be discouraged because it presupposes a nonpolar σ core, which will generally not be the case when heteroatoms are present.

The Crystal Structures of Two Novel Polycyclic Products, $C_{26}H_{26}O_2$ and $C_{24}H_{10}$, from the Photolysis of *anti*-[2.2]Paracyclonaphthane

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Received September 11, 1967

Abstract: X-Ray crystallographic techniques employing the symbolic addition procedure for phase determination have been used to elucidate the structures of two polycyclic products from the photolysis of *anti*-[2.2]paracyclonaphthane, a dibenzodimethoxy compound (II) and dibenzoequinene (IV), a centrosymmetrical hydrocarbon. Both molecules crystallize in space group $P2_1/n$ with cell parameters $a = 7.88 \pm 0.02$ Å, $b = 16.17 \pm 0.02$ Å, $c = 14.92 \pm 0.02$ Å, $\beta = 91°57' \pm 15'$ for II, and $a = 10.14 \pm 0.02$ Å, $b = 7.90 \pm 0.02$ Å, $c = 10.07 \pm 0.02$ Å, $\beta = 101°30' \pm 15'$ for IV. The six-membered rings which form *via* the internal Diels–Alder reaction of the inner rings of naphthalene system all have the boat conformation. The cyclobutane ring in IV is highly puckered with a dihedral angle of 124.5° and an average C–C bond length of 1.576 Å.

In the course of their investigations of the reactions of singlet oxygen with strained aromatic systems, Wasserman and Keehn[2] have found that the photosensitized autoxidation of *anti*-[2.2]paracyclonaphthane leads to two novel polycyclic products, a dibenzodimethoxy polycyclic (II) and the centrosymmetrical hydrocarbon, dibenzoequinene (IV). The major product of the photoxidation reaction is II while IV is observed as a minor product. Recently, however, IV has been found to be the main product in the purely photochemical reaction in the absence of oxygen.[2b]

It is believed that the photoxidation reaction proceeds in several stages. The first step involves the addition of singlet oxygen to the naphthalene system to form a transannular peroxide followed by a second-stage internal Diels–Alder reaction. Solvolysis in methanol leads to II. Dibenzoequinene (IV) appears to form by a light-induced intramolecular cyclization possibly through the intermediate III. Naphthalene normally does not add oxygen in the manner described above; however, the strain associated with the out-of-plane distortions of the naphthalene rings is thought to impart greater reactivity to the dienoid system. Such ring deformations have been demonstrated in similar systems. For example, Gantzel and Trueblood[3] have reported the X-ray structure determination of [3.3]-paracyclophane in which the aromatic rings are deformed slightly into a symmetrical boat form, the bending being about 6° at each end. Out-of-plane

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