Coulomb integrals $[ii \mid jj]$ was necessary in order to obtain good agreement with experiment.[2] In this Note, it is shown that, within the formalism suggested by Ruedenberg, a different determination of ζ and ζ^C is possible, which leads to acceptable agreement between the predicted and observed properties of benzene, *without any ad hoc adjustment of theoretically computed integrals*:

(1) The potential $U_i^C(\zeta^C)$ has been replaced by $W_i(\zeta, \zeta^C)$:

$$W_i = U_i^C + e^2[(\phi_i(\zeta))^2 \mid - e^2[(\phi_i(\zeta^C))^2 \mid,$$

because it is inconsistent to use two different exponents in describing the same $2p_z$ distribution.

(2) The separations between the lower excited electronic states of benzene have been calculated[3] in the manner described by Ruedenberg. The values given in Table I are purely theoretical, and are determined by the value of ζ. Evidently, values of ζ in the region of 1.2 lead to reasonable agreement with experiment.

(3) When a value of ζ is assumed and the integrals $[ii \mid jj]$ and overlap integrals determined, the value of the resonance integral γ can be deduced[3] from each of the spectroscopic transition energies. With $\zeta = 1.2$, one obtains the following values (in electron volts) for γ:

-1.45 $({}^1A_{1g} \to {}^1E_{1u})$; -2.05 $({}^1A_{1g} \to {}^1B_{2u})$;

-2.12 $({}^1A_{1g} \to {}^3B_{1u})$; -2.17 $({}^1A_{1g} \to {}^3E_{1u})$;

-2.31 $({}^1A_{1g} \to {}^1B_{1u})$.

The mean value is $\bar{\gamma} = -2.02$ eV. This semiempirical result is not very sensitive to the value of ζ assumed for its derivation. Thus, with $\zeta = 1.6$, $\bar{\gamma} = -2.31$, the individual values of γ being scattered in the range $-2.93 \leq \gamma \leq -1.30$ eV.

(4) Theoretical values of γ have been calculated,[3] using the assumed potential $W(\zeta, \zeta^C)$: calculations have been carried out for the values of ζ and ζ^C in the range 1.0 to 1.6, at intervals of 0.05. Some results are this approach, however, empirical adjustment of shown in Table II. This table also shows the theoretical values of the electron affinity and ionization potential calculated[3] in the manner described by Ruedenberg.[1,2] Best agreement between theory and experiment is obtained with $\zeta \approx 1.2$, $\zeta^C \approx 1.4$, the agreement being as good as could be expected with the present orbital approximation. On the other hand, with the Ruedenberg values of ζ and ζ^C quoted above, (a) the calculated spacings of the excited electronic levels are in all cases about 100% too large; (b) the calculated ionization potential is about 7 eV too large; (c) the electron affinity is predicted to have the very unlikely value of 4.7 eV.

TABLE I. Separation (in electron volts) between excited electronic levels of benzene.

Separation	$\zeta=1.0$	$\zeta=1.2$	$\zeta=1.4$	$\zeta=1.6$	Exptl[a]
${}^1E_{1u}-{}^3B_{1u}$	4.16	4.96	5.81	6.70	3.2
${}^1B_{1u}-{}^3B_{1u}$	1.16	1.91	2.80	3.81	2.4
${}^1B_{2u}-{}^3B_{1u}$	0.81	1.29	1.85	2.44	1.1
${}^3E_{1u}-{}^3B_{1u}$	0.41	0.65	0.93	1.22	0.7

[a] Theory refers to (0, 0) transitions, which are difficult to locate experimentally. Experimental data are taken from M. J. S. Dewar and N. Sabelli, J. Phys. Chem. **66**, 2310 (1962) with the following exceptions: (a) $\Delta E({}^1A_{1g} \to {}^3B_{1u}$ is taken as 3.8 eV instead of the more usual 3.6 eV, to allow for distortion in the triplet state [J. De Heer and R. Pauncz, J. Chem. Phys. **39**, 2314 (1963)]; (b) $\Delta E({}^1A_{1g} \to {}^3E_{1u})$ is taken as 4.5 eV [S. D. Colson and R. D. Bernstein, J. Chem. Phys. **43**, 2661 (1965)].

TABLE II. Results of calculations (all energies in electron volts).

ζ	1.2	1.2	1.3	1.3	1.6
ζ^c	1.4	1.5	1.4	1.5	1.1
γ[a]	−1.67	−1.85	−2.01	−2.19	−2.22
I	9.62	8.30	9.67	8.19	16.72
A	−1.15	−2.93	−1.89	−3.97	+4.67

[a] γ is the purely theoretical value of the resonance integral. I and A are the theoretical values of the ionization potential and electron affinity of benzene, which may be compared with the experimental value [R. E. Honig, J. Chem. Phys. **16**, 105 (1948)] $I = 9.43$ eV and the estimated [N. S. Hush and J. A. Pople, Trans. Faraday Soc. **51**, 600 (1955)] $A \approx -0.54$ eV.

(5) The integral $\langle \phi_i \mid \mathcal{H}_i^C \mid \phi_i \rangle$ is sensitive to the choice of values of ζ and ζ^C; with $\zeta = 1.2$ and $\zeta^C = 1.4$, its value is 4.30 eV. It has been customary to equate $\langle \phi_i \mid \mathcal{H}_i^C \mid \phi_i \rangle$ to the negative of the sp^3 valence state p-electron affinity of carbon (~0.5 eV), *but the present results indicate that this cannot be done.* This is due partly to the noninclusion of exchange operators in $\mathcal{H}_i^C$, and partly to the fact that an electronic structure derived with $2s$, $2p_x$, $2p_y$ (but not $2p_z$) orbitals as functions of the same exponent ζ^C must be a poor approximation to the "valence state" in the sense that Mulliken[4] used the term.

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[3] To avoid possible error for small values of ζ, integrals dependent on overlap between nonneighboring atoms have been *included* throughout the calculations reported in this note. See Ref. 1, pp. 1878–1883.

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Dipole Moment of Difluorophosphine

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THE recently reported[1] compound, difluorophosphine, F_2HP, is a much stronger electron-pair donor than either PH_3 or PF_3. As a result, the borane addition compound of F_2HP, F_2HPBH_3, is significantly less dissociated at 25°C than are the related compounds,

TABLE I. Data for determination of dipole moment of gaseous F_2HP.[a]

T (°K)	$(\Delta C/\Delta P_{P\to 0})$ $[(\mu\mu F/mm)\times 10^3]$	P_T (cc)
299.01	1.649	48.06
287.56	1.774	49.70
277.24	1.876	50.69
267.90	2.002	52.26
258.77	2.133	53.79
250.61	2.268	55.38

[a] Polarization$_{(\text{atomic+electronic})}=10.7\pm1.3$ cc; $C_s=213.3\pm0.5$; slope of line P_T vs $(1/T)=11\,170\pm340$.

H_3BPH_3 and H_3BPF_3.[2] A recently completed investigation of some of the physical characteristics of F_2HP shows further that the molecule has a significantly *larger* dipole moment ($\mu=1.35\pm0.02$ D) than either F_3P ($\mu=1.025$ D)[3] or H_3P ($\mu=0.579$).[4]

Gaseous F_2HP was prepared by methods reported earlier.[1] The dielectric constant of HPF_2 gas was measured as a function of temperature using a conventional heterodyne beat system,[5] operating at 1 Mc/sec over the temperature range 250.61°–299.01°K. The capacitance cell used was like that described by Holmes and Carter.[6] Its capacitance was determined using NH_3 gas as a standard, the value of 1.468 D being taken as the dipole moment and 5.3 cc as the temperature-independent part of the polarization.[7] Pertinent data are summarized in Table I. The dipole moment was obtained by the standard Debye method.

Values for the P–H and P–F bond moments can be calculated from the geometry and known dipole values for PH_3 and PF_3 if one assumes that the lone pair moment in each case is negligible.[8] If the measured F–P–F angle of 98.2±0.6° in PF_3[9] is used, the P–F bond moment can be calculated as 0.71 D. Similar calculations for PH_3 using the known HPH bond angle of 93.3°[10] give a P–H bond moment of 0.36 D. Addition of these vectors at the PF_3 angle gives a resultant of 1.09 D for the molecule F_2HP. Addition of the vectors at the PH_3 angle gives a resultant of 1.08 D. Clearly, small changes in molecular geometry are not adequate to account for the discrepancy between the calculated moment and the observed value of 1.35±0.02 D.

Agreement between measured and calculated values can be obtained if it is assumed that slight changes in the P–F bond moment occur when fluorines in PF_3 are replaced by hydrogens in the sequence $PF_{3-x}H_x$. If a reasonable FPF angle of 96° is assumed in F_2HP and the value of the P–H bond moment is assumed to be constant in the series at a value of 0.36 D, the value of μ_{P-F} calculated for HPF_2 is 0.94 D. In an earlier report on the dipole moments of the alkyl phosphines,[8] it was necessary to assume stepwise change in the P–R moment as one proceeds from PR_3 to PRH_2. This same procedure is required in the present study. Values for the two cases are summarized in Table II. It is appropriate to note, however, that in the calculations of the alkyl phosphines, the phosphorus was assumed to be the negative end of the dipole vector, while in the fluorophosphines the fluorine was assumed to be negative with respect to phosphorus and hydrogen positive relative to phosphorus.

The reproducibility of the trends is striking. The compound H_2PF has not yet been synthesized but the extrapolated P–F moment from Table II can be used to *estimate* the over-all moment of the still unknown molecule H_2FP as 1.30 D.

TABLE II. Empirical values of P–R bond moments which by vector addition give measured moments of alkyl phosphines and fluorophosphines.

Compound	R= $-CH_3$	$-C_2H_5$	$-F$
PH_2R	1.06 D	1.17 D	1.15[a]
PHR_2	0.95	1.06	0.94
PR_3	0.83	0.94	0.71

[a] Estimated.

A qualitative electronic argument to rationalize the empirically observed trend in P–F moments can be given. In PF_3 each highly electronegative fluorine atom competes with two other fluorines for negative charge from the phosphorus. Replacement of a fluorine by a less electronegative hydrogen permits greater migration of charge from phosphorus toward the two competing fluorines thus increasing the net P–F bond moment in HPF_2.

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