Theoret. chim. Acta (Berl.) 13, 56—64 (1969)

Semi-Empirical π-Electron Calculations

MARGARET L. BAILEY
Mathematical Institute, University of Oxford

Received September 20, 1968

Using a method for calculating the off-diagonal core integrals based on the gradient of the overlap integrals, the parameterization of the PPP SCF MO method for π-electron molecules has been studied. The transition energies obtained for benzene-like heterocycles are in satisfactory agreement with experimental absorption spectra values.

Mit einer Methode zur Berechnung der nicht-diagonalen Kernintegrale mit Hilfe des Gradienten der Überlappungsintegrale wird die Parameterisierung der PPP SCF MO-Methode für π-Elektronen-Moleküle studiert. Die für benzolähnliche Heterocyclen erhaltenen Übergangsenergien stimmen befriedigend mit experimentellen Werten aus Absorptionsmessungen überein.

Etude de la paramétrisation de la méthode PPP SCF MO pour électrons π, en utilisant une méthode de calcul de éléments de coeur non diagonaux fondée sur le gradient des intégrales de recouvrement. Les énergies de transition obtenues pour les hétérocycles benzéniques sont en accord satisfaisant avec l'expérience.

Introduction

The interpretation of experimental absorption spectra of aromatic molecules has been successfully accomplished by the Pariser-Parr-Pople semi-empirical SCF MO method for π-electron systems; however, the parameters required are usually determined by comparison of the singlet transition energies with the experimental spectra for a given "test" molecule, these parameters then being used to calculate the spectra of a series of related molecules. In this paper the question of just one parameterization for many different types of molecules, without recourse to experimental spectra, is considered. Calculations of the singlet transition energies of over twenty single-ring heterocycles have been carried out using a method which requires no arbitrary parameterization. For the wide range of molecules studied, the transition energies are in satisfactory agreement with experimental spectra, and compare favourably with results obtained using the conventional means of parameterization for just one particular series of related molecules.

Method and Parameters

The method used is similar to that described by Pariser, Parr and Pople [1]. The molecular orbitals ψ_i are expressed as

$$\psi_i = \sum_{u=1}^{n} C_{ui} \phi_u ,$$

where ϕ_u is a π-type $2p$-atomic orbital centred on atom u and n is the number of atoms contributing π-electrons to the conjugated system. The coefficients C_{ui}

of the MO matrix are the solutions of the equations

$$\sum_v F_{uv} C_{vi} = E_i \sum_v S_{uv} C_{vi} ,$$

where the F_{uv} are the elements of the Hartree-Fock matrix (F matrix) and the E_i are the orbital energies. The F matrix elements, after simplification [2], are

$$F_{uu} = U_{uu} + \tfrac{1}{2} P_{uu} \gamma_{uu} + \sum_{p \neq u} (P_{pp} - Z_p) \gamma_{up} ,$$

$$F_{uv} = U_{uv} - \tfrac{1}{2} P_{uv} \gamma_{uv} , \qquad (u \neq v) ,$$

where U_{uv}, γ_{uv} and P_{uv} are elements of the core, repulsion and bond-order matrix respectively, and Z_p is the "effective charge" of the framework ion. The configurational wavefunctions $\chi_{i \to k}$ in which an electron is excited from an occupied MO ψ_i to an unoccupied MO ψ_k are used to obtain the configuration-interaction matrix elements

$$\langle \chi_{i \to k} | H | \chi_{j \to l} \rangle = \delta_{ij} \delta_{kl} (E_k - E_i) + \sum_{u,v} (2 C_{uj} C_{ul} C_{vi} C_{vk} - C_{ui} C_{uj} C_{vk} C_{vl}) \gamma_{uv} .$$

All possible single excitations are included. The eigenvalues of this matrix, measured relative to the ground state, yield the singlet transition energies.

The two-centre repulsion integrals γ_{uv} were calculated using the Nishimoto-Mataga approximation [3],

$$\gamma_{uv} = e^2 / (R_{uv} + a_{uv}) , \qquad a_{uv} = 2e^2 / (\gamma_{uu} + \gamma_{vv}) ,$$

where R_{uv} is the distance between atoms u and v and γ_{uu} is the one-centre repulsion integral (γ parameter).

The two-centre core integrals (β integrals) U_{uv} were calculated from the gradient of the overlap integrals [4]. From Heisenberg's equation of motion for the position operator $\boldsymbol{r}$,

$$i\hbar \, d\boldsymbol{r}/dt = [\boldsymbol{r}, H] = i\hbar \, \boldsymbol{p}/m ,$$

where $\boldsymbol{p}$ is the momentum operator and H is the Hamiltonian for the π-electrons, an expression relating the off-diagonal core matrix elements to the linear momentum matrix elements, within the approximations of the PPP theory, is obtained

$$i\hbar \, \boldsymbol{p}_{rs}/m = U_{rs} (\boldsymbol{R}_r - \boldsymbol{R}_s) .$$

For a planar molecule, this reduces to

$$U_{rs} = (\hbar^2/m) R^{-1} dS/dR .$$

By specifying the orbitals to be used in calculating dS/dR, the off-diagonal core matrix elements can be computed explicitly. Both Slater orbitals and double-ζ orbitals were used. For the former the exponents were obtained from Slater's rules [5]; for the latter the values of Clementi [6] were used. Only nearest neighbour β's were considered.

Since the β's depend explicitly on the bond length, the results will depend on the choice of geometry for the molecule. Where possible, geometries were obtained from experiment; if these were not available, an appropriate geometry was assumed by using data for similar molecules.

For comparison, the β integrals were also calculated using the Nishimoto-Forster variable-β approximation [7], which relates the core matrix to the bond-order matrix

$$U_{uv} = A_0 + A_1 P_{uv} .$$

The A_0 and A_1 parameters were taken from Nishimoto and Forster [8].

For atoms contributing one electron to the π-system (singly-charged core), the choice of values for core and γ parameters is well established. The core parameter (α parameter) has been evaluated using the Goeppert-Mayer and Sklar approximation [9],

$$U_{uu} = -I_u ,$$

where I_u is the valence-state ionization potential. The γ parameter has been approximated by the formula given by Pariser and Parr [10],

$$\gamma_{uu} = I_u - A_u ,$$

where A_u is the valence-state electron affinity. Two sets of parameters were used, the first being calculated from the valence-state data of Pilcher and Skinner [11], the second from the more commonly used data of Hinze and Jaffé [12]. The values are given in Table 1.

For atoms contributing two electrons to the π-system (doubly-charged core), the values are not so well defined. An analogous method to that used above has been suggested with the neutral atom replaced by the positive ion, in which the second and first ionization potentials are used instead of the valence-state ionization potential and electron affinity. Although this gives satisfactory values for the γ parameter, the values obtained for the core parameter did not lead to reasonable results. This may be due to the difference between the ionization potentials of a neutral atom and of a molecule containing that atom being large, this having been attributed to charge transfer effects [11]. To overcome this problem, the approximation discussed by Kwiatkowski [13] was used. The ionization potential is written

$$I_u = \Delta E(X \rightarrow X^{+}) + \gamma_{uu} ,$$

where X stands for the doubly-charged core atom in the appropriate valence state. The first term in this expression was replaced by the ionization potential of CH_3NH_2 for nitrogen and CH_3OH for oxygen, since these contain the given atom in the appropriate state. The values of the ionization potentials were taken from Turner [14]. The valence-state data of Hinze and Jaffé [12] was used, the parameters being given in Table 1.

The parameters used in the variable-β method were taken from Nishimoto and Forster [8]. For singly-charged core atoms, the values are those calculated from the data of Hinze and Jaffé, but different values are calculated for the doubly-charged core atoms. These values are given in Table 1.

The formula used in calculating the Slater exponent does not distinguish between singly- and doubly-charged core atoms. If the doubly-charged core atom is considered as being derived from the positive ion, a different Slater exponent is calculated. Both values were used, these being given in Table 1.

The oscillator strengths were calculated by both the dipole-length and dipole-velocity formulae [15]. The final value was obtained by taking the geometrical mean of these two quantities, as suggested by Hansen [16].

The calculations were programmed in ALGOL and run on the University of Oxford English Electric KDF 9 computer.

Table 1. *Parameters used in the calculations*

	Ċ	Ṅ	N̈	Ȯ	Ö
U_{uu} (core parameter)					
A	−11.22	−14.51		−17.25	
B	−11.16	−14.12	−25.73	−17.70	−30.07
C	−11.16	−14.12	−26.70	−17.70	−32.90
γ_{uu} (gamma parameter)					
A	10.60	13.31		14.67	
B	11.13	12.34	16.76	15.23	19.24
C	11.13	12.34	17.44	15.23	21.53
ζ (Slater exponent)					
1	3.25	3.90	3.90	4.55	4.55
2	3.25	3.90	4.25	4.55	4.90

Set *A* is calculated from the data of Pilcher and Skinner [11].
Set *B* is calculated from the data of Hinze and Jaffé [12].
Set *C* is taken from Nishimoto and Forster [8].

Results and Discussion

The transition energies obtained after configuration interaction, and the oscillator strengths, for various benzene derivatives are given in Table 2, together with the appropriate experimental absorption spectra values. Where the experimental molecular geometry was used, the reference is given with the name of the molecule. For those molecules for which the geometry was estimated, the bond lengths used are given. For substituted molecules such as phenylenediamines and aminopyridines, the ring was assumed to have the same geometry as the parent molecule, benzene or pyridine in these two cases. The external group may have some effect on the neighbouring C–C bond length, this being more pronounced for groups in the ortho position. The NH_2 group has been assumed to lie in the plane of the molecule, as usual, but the use of the ionization potential of CH_3NH_2 to calculate the core parameter has been assumed to overcome any effects arising from the non-planarity of the NH_2 group. The $C–NH_2$ and C–OH bond lengths have been taken as 1.38 Å and 1.36 Å respectively.

The transition energies obtained are in good agreement with experimental spectra – considering that the method contains no adjustable parameters, the results are very satisfactory. A disadvantage is that many of the molecular geometries are not available from experiment, and those available are often inaccurate. Even for molecules where the experimental geometry is not known, a reasonable

Table 2. *Transition energies (eV) and oscillator strengths*

L	*N*	Expt.		
Benzene [18]		[19]	[20]	[21]
4.85±.04 (0.0)	4.89 (0.0)	4.89 (0.01)	4.77	4.88 (0.001)
6.09±.07 (0.0)	6.18 (0.0)	6.17 (0.126)	6.05	6.14 (0.10)
6.92±.07 (0.55)	7.01 (1.19)	6.98 (1.035)	6.70	6.74 (0.69)
Pyridine [22]		[23]	[24]	[21]
4.89±.03 (0.016)	4.98 (0.06)	4.93 (0.032)	4.75 (0.04)	4.96 (0.03)
6.18±.05 (0.009)	6.30 (0.04)	6.28 (0.122)	6.17 (0.10)	6.36 (0.20)
7.05±.07 (0.49)	7.24 (1.13)	6.96 (0.66)	6.94 (1.30)	7.04 (1.36)
7.12±.03 (0.54)	7.17 (1.13)			
Pyridazine [25] (with $R_{\mathrm{C-C}} = 1.38$ Å)		[23]	[21]	
5.01±.01 (0.014)		5.04 (0.018)	5.01 (0.020)	
6.25±.02 (0.004)		6.52 (*s*)	6.38 (0.10)	
7.08±.03 (0.50)		6.89 (0.15)		
7.31±.03 (0.53)				
Pyrimidine [26]		[23]	[21]	
5.07±.02 (0.019)	5.16 (0.07)	5.07 (0.024)	5.13 (0.052)	
6.38±.04 (0.020)	6.50 (0.09)	6.61 (*s*)	6.57 (0.16)	
7.21±.02 (0.48)	7.44 (1.09)	~7.21	>7.31	
7.41±.03 (0.53)	7.49 (1.12)			
Pyrazine [27]		[23]	[21]	[28]
4.82±.03 (0.049)	4.95 (0.18)	4.75 (0.084)	4.82 (0.10)	4.77
6.34±.05 (0.026)	6.39 (0.20)	6.38 (0.119)	6.42 (0.145)	
7.36±.05 (0.51)	7.59 (0.98)	>7.2	>7.31	
7.55±.01 (0.48)	7.77 (1.11)			
Sym-triazine [8]		[23]	[28]	[29]
5.20±.03 (0.0)	5.48 (0.0)	5.58 (0.004)	5.29	
6.58±.02 (0.0)	6.89 (0.0)			6.92
7.32±.01 (0.52)	7.60 (1.19)	>7.2		
Sym-tetrazine [30]		[23]		
4.84±.05 (0.045)		4.92 (0.05)		
6.47±.03 (0.011)				
7.14±.06 (0.46)				
7.83±.04 (0.55)				
p-benzoquinone [31]		[32]	[33]	
4.17±.08 (0.0)	3.59 (0.0)	4.28	4.20 (0.008)^{c}	
4.83±.06 (0.49)	4.51 (0.85)	5.07	5.04 (0.46)	
6.68±.13 (0.0)	6.28 (0.0)			
6.69±.05 (0.0)	6.61 (0.0)			
7.17±.02 (0.10)	7.10 (0.20)			
Aniline (as benzene with $R_{\mathrm{C-N}} = 1.38$ Å)		[19]	[21]	
4.38±.04 (0.02)	4.40 (0.06)	4.40 (0.028)		
5.29±.05 (0.20)	5.38 (0.40)	5.39 (0.14)	5.27	
6.27±.05 (0.17)	6.41 (0.52)	6.40 (0.51)	6.30	
6.59±.03 (0.36)	6.68 (0.90)	6.88 (0.57)	>7.07	
7.50±.04 (0.32)	7.67 (0.49)	7.87 (~0.68)		
7.60±.05 (0.02)	7.62 (0.01)			

Table 2 (continued)

L	N	Expt.			
o-phenylenediamine (as aniline)		[34]			[35]
4.13 ± .04 (0.04)	4.13 (0.09)	4.21 (0.039)			4.29^b
4.82 ± .06 (0.11)	4.87 (0.26)	5.19 (0.11)			5.26
5.87 ± .05 (0.47)	6.02 (1.10)	5.69			
5.91 ± .06 (0.13)	6.04 (0.40)				
m-phenylenediamine (as aniline)		[34]			[35]
4.24 ± .04 (0.015)	4.24 (0.04)	4.21 (0.04)			4.23^b
5.17 ± .04 (0.07)	5.25 (0.14)	5.20 (0.19)			5.17
5.63 ± .07 (0.52)	5.81 (1.22)	5.63			
5.65 ± .07 (0.16)	5.77 (0.46)				
p-phenylenediamine (as aniline)		[34]			[35]
3.94 ± .06 (0.04)	3.92 (0.13)	4.05 (0.038)			3.94^b
4.94 ± .05 (0.30)	5.00 (0.62)	5.08 (0.17)			5.04
5.99 ± .10 (0.0)	6.27 (0.0)	6.14			
6.39 ± .12 (0.0)	6.75 (0.0)				
6.44 ± .04 (0.20)	6.57 (0.56)				
6.61 ± .03 (0.42)	6.67 (0.96)				
2-aminopyridine (as pyridine)		[36]			
4.36 ± .03 (0.06)	4.45 (0.14)	4.19^a	4.30^b	4.32^c	
5.44 ± .05 (0.19)	5.57 (0.43)	5.39	5.37	5.41	
6.45 ± .07 (0.08)	6.75 (0.36)				
6.73 ± .02 (0.33)	6.91 (0.81)				
3-aminopyridine (as pyridine)		[36]			[37]
4.24 ± .04 (0.04)	4.33 (0.13)	4.20^a	4.25^b	4.30^c	4.11^a
5.25 ± .05 (0.17)	5.36 (0.40)	5.28	5.34	5.37	5.14
6.22 ± .06 (0.14)	6.45 (0.43)				5.88
6.75 ± .02 (0.31)	6.91 (0.79)				
4-aminopyridine (as pyridine)		[36]			
4.62 ± .03 (0.002)	4.68 (0.007)	4.59^a	4.77^b	4.68^c	
5.25 ± .05 (0.20)	5.41 (0.39)	5.04	5.32	5.14	
6.11 ± .04 (0.23)	6.30 (0.61)				
6.63 ± .03 (0.36)	6.70 (0.91)				
2-aminopyrimidine (as pyrimidine)		[36]			
4.44 ± .04 (0.05)	4.54 (0.15)	4.19^a	4.38^b	4.25^c	
5.62 ± .06 (0.24)	5.82 (0.56)	5.49	5.56	5.53	
6.52 ± .09 (0.003)	6.97 (0.08)				
6.93 ± .02 (0.30)	7.23 (0.77)				
4-aminopyrimidine (as pyrimidine)		[36]			
4.69 ± .03 (0.05)	4.78 (0.10)	4.52^a	4.71^b	4.63^c	
5.49 ± .06 (0.19)	5.65 (0.40)	5.25	5.44	5.32	
6.37 ± .05 (0.17)	6.66 (0.54)				
6.86 ± .02 (0.31)	7.00 (0.79)				
5-aminopyrimidine (as pyrimidine)		[38]			
4.16 ± .05 (0.05)	4.27 (0.16)	3.94^a	4.16^c		
5.24 ± .05 (0.19)	5.34 (0.48)	5.04	5.25		
6.41 ± .08 (0.02)	6.80 (0.12)				
6.95 ± .02 (0.33)	7.20 (0.67)				

Table 2 (continued)

L	*N*	Expt.		
Phenol (as benzene with $R_{\mathrm{C-O}} = 1.36$ Å)		[39]	[21]	
$4.65 \pm .05$ (0.009)	4.62 (0.04)	4.59 (0.023)	4.55	
$5.72 \pm .06$ (0.10)	5.75 (0.21)	5.78 (0.175)	5.83	
$6.64 \pm .05$ (0.37)	6.71 (0.89)	6.68 (0.585)	6.53	
$6.70 \pm .03$ (0.47)	6.78 (1.12)	6.90 (0.371)		
Catechol (as phenol)		[40]		
$4.50 \pm .06$ (0.014)	4.43 (0.05)	4.43, 4.52^b		
$5.42 \pm .08$ (0.07)	5.39 (0.18)	5.79		
$6.29 \pm .07$ (0.52)	6.41 (1.20)			
$6.41 \pm .06$ (0.32)	6.44 (0.77)			
Resorcinol (as phenol)		[41]	[40]	
$4.53 \pm .05$ (0.008)	4.49 (0.03)	4.49^a	4.44, 4.53^b	
$5.57 \pm .06$ (0.04)	5.60 (0.09)	5.64	5.71	
$6.22 \pm .09$ (0.55)	6.37 (1.31)			
$6.35 \pm .08$ (0.33)	6.35 (0.79)			
Hydroquinone (as phenol)		[42]	[40]	[21]
$4.42 \pm .07$ (0.03)	4.29 (0.10)	4.23	4.25, 4.29^b	
$5.45 \pm .08$ (0.19)	5.47 (0.40)	5.51	5.56	5.42
$6.63 \pm .04$ (0.36)	6.74 (0.83)			6.52
$6.68 \pm .03$ (0.48)	6.74 (1.10)			

Abbreviations used in the Table:
L calculation using the Linderberg beta method.
N calculation using the Nishimoto-Forster variable-beta method.
a, *b*, *c* indicate the solvent the spectra were measured in, ethanol, cyclohexane and water respectively.

estimate leads to satisfactory results. One notable success is in the results for *p*-benzoquinone, a molecule for which most other PPP calculations have given poor agreement with experiment. This may be a consequence of using the molecular geometry, which shows that the bonds alternate as in a conjugated chain, rather than of assuming a benzene-like geometry. An advantage of the Nishimoto-Forster variable-β method is that it assumes a regular geometry, thus avoiding the problem of getting accurate bond distances and bond angles. However, its parameters are determined from experimental spectra, and, as the experimental values given in Table 2 show, these spectra can differ appreciably for the same molecule under different experimental conditions.

The transition energies do not change significantly with the type of orbital used, although the double-ζ orbitals tend to give lower values for the first transitions. The different sets of parameters also do not bring about much change in the transition energies. No one of the sets seems to be superior. The two different values used for the Slater exponent of doubly-charged core atoms give almost the same value for the first transition energy, with small changes in the higher energies. This suggests that the bond distance is the important factor in calculating the β integrals.

The results for ortho-substituted molecules do not agree with experiment as well as those for meta- and para-substituted molecules. This may be a consequence of the geometry used in the calculation, as previously mentioned. It has been assumed that the aminopyridines and aminopyrimidines exist mainly in the amino form in solution, which has been shown experimentally [17].

The oscillator strengths obtained by the three different methods show the same trends. The geometrical mean method does not include an energy factor, thus avoiding the problem of whether to use calculated or experimental values.

The results for these calculations have been presented as the mean and standard deviation of the transition energies obtained for the different sets of parameters, and the mean of the oscillator strengths, for the calculations using the Linderberg method for determining the β integrals.

Conclusion

A method by which the off-diagonal core integrals are calculated from the gradient of the overlap integrals, together with a set of parameters calculated from valence-state data, has led to a satisfactory interpretation of experimental absorption spectra.

Acknowledgement. The author wishes to thank Professor C. A. Coulson, F.R.S., for helpful discussions, and acknowledges financial assistance from a Shirtcliffe Fellowship.

References

1. Parr, R. G.: Quantum theory of molecular electronic structure. New York: W. A. Benjamin, Inc. 1963.
2. Pople, J. A.: Trans. Faraday Soc. **49**, 1375 (1953).
3. Nishimoto, K., and N. Mataga: Z. physik. Chem. (Frankfurt) **12**, 335 (1957).
4. Linderberg, J.: Chem. Phys. Letters **1**, 39 (1967).
5. Slater, J. C.: Physic. Rev. **36**, 57 (1930).
6. Clementi, E.: IBM Research Paper RJ-256 (1963).
7. Nishimoto, K., and L. S. Forster: Theoret. chim. Acta (Berl.) **3**, 407 (1965).
8. — — Theoret. chim. Acta (Berl.) **4**, 155 (1966).
9. Goeppert-Mayer, M., and A. L. Sklar: J. chem. Physics **6**, 645 (1938).
10. Pariser, R., and R. G. Parr: J. chem. Physics **21**, 466 (1953).
11. Pilcher, G., and H. A. Skinner: J. inorg. nucl. Chem. **24**, 937 (1962).
12. Hinze, J., and H. H. Jaffé: J. Amer. chem. Soc. **84**, 540 (1962).
13. Kwiatkowski, S.: Acta physica polon. **29**, 477 (1966).
14. Turner, D. W.: Advan. physic. org. Chem. **4**, 31 (1966).
15. Ehrenson, S., and P. E. Phillipson: J. chem. Physics **34**, 1224 (1961).
16. Hansen, A. E.: Molecular Physics **13**, 425 (1967).
17. Anderson, L. C., and N. V. Seegar: J. Amer. chem. Soc. **71**, 340 (1949); — Brown, D. J., E. Hoerger, and S. F. Mason: J. chem. Soc. (London) **1955**, 1035.
18. Langseth, A., and B. P. Stoicheff: Canad. J. Physics **34**, 350 (1956); — K. Kimura, and M. Kubo: J. chem. Physics **32**, 1776 (1960).
19. Kimura, K., H. Tsubomura, and S. Nagakura: Bull. chem. Soc. Japan **37**, 1336 (1964).
20. Petruska, J.: J. chem. Physics **34**, 1120 (1961).
21. Klevens, H. B., and J. R. Platt: ONR Technical Report, Laboratory of Molecular Structure and Spectra, University of Chicago, part 1, p. 145 (1953—1954).
22. Bak, B.: Private communication to W. C. Mackrodt.
23. Favini, G., M. Simonetta, and I. F. Bellobono: Unpublished work, quoted by G. Favini, I. Vandoni, and M. Simonetta: Theoret. chim. Acta (Berl.) **3**, 418 (1965).
24. Pickett, L. W., M. E. Corning, G. M. Wieder, D. A. Semenov, and J. M. Buckley: J. Amer. chem. Soc. **75**, 1618 (1953).

25. Coulson, C. A.: J. chem. Soc. (London) **1963**, 5893.
26. Spencer, M.: Acta crystallogr. **12**, 59 (1959).
27. Sutton, L. E. (Ed.): Tables of interatomic distances and configuration in molecules and ions. London: The Chemical Society, Publication 18, 1965.
28. Halverson, F., and R. C. Hirt: J. chem. Physics **19**, 711 (1951).
29. Brinen, J. S., R. C. Hirt, and R. C. Schmitt: Spectrochim. Acta **18**, 863 (1962).
30. Bertinotti, F., G. Giacomello, and A. M. Liquori: Acta crystallogr. **9**, 510 (1956).
31. Trotter, J.: Acta crystallogr. **13**, 86 (1960).
32. Poquet, B.: Thèse de Troisième Cycle. Bordeaux 1958, quoted by C. Leibovici, and J. Deschamps: Theoret. chim. Acta (Berl.) **4**, 321 (1966).
33. Brand, J. C. D., and T. H. Goodwin: Trans. Faraday Soc. **53**, 295 (1957).
34. Godfrey, M., and J. N. Murrell: Proc. Roy. Soc. (London) A **278**, 71 (1964).
35. Forbes, W. F., and I. R. Leckie: Canad. J. Chem. **36**, 1371 (1958).
36. Mason, S. F.: J. chem. Soc. (London) **1960**, 219.
37. Okuda, S.: Pharm. Bull. (Tokyo) **4**, 257 (1956).
38. Boarland, M. P. V., and J. F. W. McOmie: J. chem. Soc. (London) 3716 (1952).
39. Kimura, K., and S. Nagakura: Molecular Physics **9**, 117 (1965).
40. Dearden, J. C., and W. F. Forbes: Canad. J. Chem. **37**, 1294 (1959).
41. Musgrave, O. C.: J. chem. Soc. (London) **1956**, 4301.
42. Adams, R., and J. L. Anderson: J. Amer. chem. Soc. **72**, 5154 (1950).

Mrs. Margaret L. Bailey
Mathematical Institute
24—29 St. Giles
Oxford/England