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The electronic structure and spectra of the polyacenes

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Abstract. This paper reports some self-consistent field molecular orbital calculations on the first nine members of the polyacene series. It is predicted that the lowest singlet band in the electronic spectrum will converge to a limit of about 18 000 $\bar{\nu}$ in the higher members of the series. The charges and bond orders are given for the first five members of the series.

1. Introduction

The work reported here was undertaken in an attempt to understand the effects of increasing conjugation in polyacene molecules. Much recent work has been done on the polyenes, and in particular it has been shown that the energy differences associated with the lowest band of the electronic spectrum converges to a limit which is not zero with increasing chain length. One of the objects of this work is to see if a similar situation exists in the polyacenes. The results obtained here are compared with those obtained by Pariser (1956), who used Hückel orbitals and extensive configuration interaction in his work on the polyacenes.

Calculations on the polyacenes were made using the self-consistent field molecular orbital method in the form given by McWeeny (1956). The electronic spectra were calculated using nine configurations arising from singly excited configurations involving the top three filled and the bottom three empty orbitals. The whole process was programmed for the University of London Mercury computer. The only data required by the machine are the coordinates of the atoms.

The results for the first nine members of the series were obtained, although only those for the first five are given here in detail. Only five members of the series are well known, the sixth has been prepared and some of its properties are known.

2. Method

The elements of the self-consistent field Hamiltonian are given by

$$h_{ii} = \omega_i + \tfrac{1}{2}P_{ii}\gamma_{ii} - \tfrac{1}{2}\gamma_{ii}^{c} + \sum_{i \neq j} (P_{jj} - Z_j)\gamma_{ij}$$

and

$$h_{ij} = \beta_{ij} - \tfrac{1}{2}P_{ij}\gamma_{ij}$$

where the $\omega_i - \Sigma_{j \neq i} Z_j \gamma_{ij}$ and the β_{ij} are the elements of the 'bare' framework Hamiltonian and the γ_{ij} are the two-electron interaction integrals $(ij|g|ij)$. We chose our energy zero as $\omega_i^{c} + \tfrac{1}{2}\gamma_{ii}^{c}$ (McWeeny and Peacock 1957), and our energy unit β as the value of the resonance integral between nearest neighbours in benzene, i.e. −4·79 ev (McWeeny and Peacock 1957).

β_{ij} was given the value −2·39 ev for nearest neighbours and zero otherwise. The two-electron integrals of the 'Coulomb' type were calculated using the method of Pariser and Parr (1953). All other two-electron integrals were set equal to zero, as we have assumed an orthonormal set of basis functions (Löwdin 1950, McWeeny 1955). All the integrals used were calculated in the machine and not printed out.

With the energy unit and zero which we have chosen several analogies with the crude Hückel-type theory appear. The diagonal elements of the Hamiltonian are all zero, which is equivalent to choosing α as the energy zero in the Hückel Hamiltonian. Furthermore, the choice of energy unit which we make gives h_{ij} for nearest neighbours values of about unity, which is analogous to the value of unity in the Hückel theory if β is chosen as the energy unit.

In calculating the excited states, transitions between six orbitals were considered, the top three occupied and the bottom three empty orbitals being used. All nine configurations involving the promotion of a single electron were considered. The energies of the first nine singlet and the first nine triplet states were calculated. The method employed is similar to that first formulated by Pople (1955) for alternant hydrocarbons. The matrix elements have the form given previously by McWeeny and Peacock (1957). We use (A) (B) ... to denote the columns of atomic orbital coefficients representing the molecular orbitals AB ... and (AB) to denote the column whose rth element is the product of corresponding elements of (A) and (B); then the energies (relative to the ground state) of the singlet and triplet functions of the configuration in which an electron has been excited from orbital I into orbital K are given by

$$ {}^{1,3}E_{IK} = (I \to K|H|I \to K) = \epsilon_K - \epsilon_I - [(II)^{\dagger}(\gamma)(KK) - (IK)^{\dagger}(\gamma)(IK)] \pm (IK)^{\dagger}(\gamma)(IK) $$

where ϵ_K, ϵ_I are the orbital energies and (γ) is the matrix of Coulomb integrals γ_{ij}. The off-diagonal elements of the configuration interaction matrix are given by

$$ {}^{1,3}(I \to K|H|J \to L) = -[(IJ)^{\dagger}(\gamma)(KL) - (LJ)^{\dagger}(\gamma)(KI)] \pm (LJ)^{\dagger}(\gamma)(KI). $$

With the exception of those of B_{2u} symmetry, it is found that the configurations interact in pairs.

The atom and bond populations in the basis of ordinary $2p_z$ atomic orbitals were calculated. The charge and bond order matrix $\mathbf{P}$ in the non-orthogonal basis is related to the matrix $\bar{\mathbf{P}}$ in the orthogonal basis in the following way (Peacock 1959)

$$ \mathbf{P} = \mathbf{S}^{-1/2}\bar{\mathbf{P}}\mathbf{S}^{-1/2} $$

where $\mathbf{S}^{-1/2}$ is the inverse square root of the matrix of overlap integrals. The populations of the atoms and bonds are given by

$$ q_{ii} = P_{ii} \quad \text{and} \quad q_{ij} = 2P_{ij}S_{ij}. $$

3. Results

In figure 1, the molecules together with the numbering of the atoms are shown. The molecular orbitals, orbital energies and the symmetries of the orbitals classified according to the representation of D_{2h} for the first five members of the series are given in table 1. To maintain consistency throughout the series for purposes of comparison, we have considered benzene to have the symmetry D_{2h} instead of its full symmetry D_{6h}. In particular, the orbital degeneracies which are group theoretic in origin appear here as accidental degeneracies.

The charges and bond orders for the first five members of the series are listed in table 2. The atom and bond populations in the non-orthogonal basis of C_{2p_z} orbitals are listed in table 2 also.

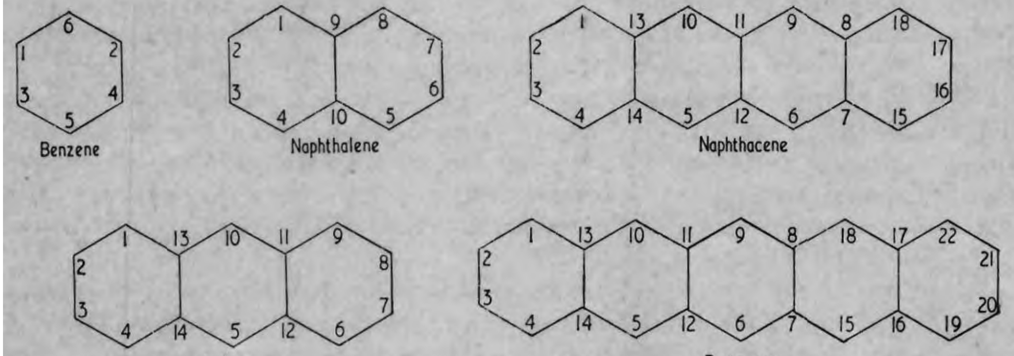

Figure 1. The molecules.

Table 1. Molecular orbitals and orbital energies for the polyacenes classified according to the representations of D_{2h}

	Benzene	Naphthalene	Anthracene	Naphthacene	Pentacene
$_{1u}$ symmetry	C 1·845β	E 2·004β	G 2·064β	I 2·092β	K 2·107β
	B'−1·178	B 1·137	E 1·457	G 1·680	I 1·814
		C'−1·382	A'−0·764	C 1·098	E 1·294
			D'−1·456	B'−1·032	A'−0·609
				F'−1·492	D'−1·187
					G'−1·512
$_{2g}$ symmetry	A 1·178	D 1·604	F 1·823	H 1·933	J 1·996
		A'−0·922	B 1·114	E 1·361	H 1·571
			C'−1·185	A'−0·673	C 1·086
				D'−1·316	B'−0·917
					F'−1·389
$_{3g}$ symmetry	B 1·178	C 1·382	D 1·456	F 1·492	G 1·512
	C'−1·845	B'−1·137	A 0·764	B 1·032	D 1·187
		E'−2·004	E'−1·457	C'−1·098	A 0·609
			G'−2·064	G'−1·680	E'−1·294
				I'−2·092	I'−1·814
					K'−2·107
$_{1u}$ symmetry	A'−1·178	A 0·922	C 1·185	D 1·316	F 1·389
		D'−1·604	B'−1·114	A 0·673	B 0·917
			F'−1·823	E'−1·361	C'−1·086
				H'−1·933	H'−1·571
					J'−1·996

The molecular orbital labels have the following significance: A, B, C ... denote the bonding rbitals in decreasing energy order and A', B', C' ... the antibonding orbitals in ascending energy rder. (For the molecular orbital coefficients see Wilkinson 1964, Ph.D. Thesis, University of ondon.)

Table 2. Charges and bond orders in the basis of orthogonalized orbitals, and atom and bond populations in the basis of ordinary $2p_z$ orbitals

Benzene

P_{11}	1·0000	q_{11}	0·7732
P_{13}	0·6667	q_{13}	0·2447

Naphthalene

P_{11}	1·0000	q_{11}	0·7857
P_{22}	1·0000	q_{22}	0·7741
P_{99}	1·0000	q_{99}	0·7507
P_{12}	0·7453	q_{12}	0·2857
P_{23}	0·5832	q_{23}	0·2008
P_{19}	0·5352	q_{19}	0·1799
$P_{9,10}$	0·5488	$q_{9,10}$	0·1934

Anthracene

P_{11}	1·0000	q_{11}	0·7899
P_{22}	1·0000	q_{22}	0·7741
$P_{10,10}$	1·0000	$q_{10,10}$	0·8015
$P_{13,13}$	1·0000	$q_{13,13}$	0·7453
P_{12}	0·7508	q_{12}	0·2886
P_{23}	0·5765	q_{23}	0·1974
$P_{1,13}$	0·5157	$q_{1,13}$	0·1692
$P_{10,13}$	0·6051	$q_{10,13}$	0·2170
$P_{13,14}$	0·5093	$q_{13,14}$	0·1717

Naphthacene

P_{11}	1·0000	q_{11}	0·7912
P_{22}	1·0000	q_{22}	0·7773
P_{55}	1·0000	q_{55}	0·8024
P_{88}	1·0000	q_{88}	0·7508
$P_{11,11}$	1·0000	$q_{11,11}$	0·7467
P_{12}	0·7733	q_{12}	0·3011
P_{23}	0·5467	q_{23}	0·1821
$P_{1,13}$	0·4929	$q_{1,13}$	0·1573
$P_{10,13}$	0·6338	$q_{10,13}$	0·2331
$P_{10,11}$	0·5760	$q_{10,11}$	0·2016
$P_{11,12}$	0·4760	$q_{11,12}$	0·1537
$P_{13,14}$	0·4913	$q_{13,14}$	0·1621

Pentacene

P_{11}	1·0000	q_{11}	0·7913
P_{22}	1·0000	q_{22}	0·7781
P_{55}	1·0000	q_{55}	0·8027
P_{66}	1·0000	q_{66}	0·8061
P_{77}	1·0000	q_{77}	0·7472
$P_{13,13}$	1·0000	$q_{13,13}$	0·7516
P_{12}	0·7783	q_{12}	0·3038
P_{23}	0·5388	q_{23}	0·1779
$P_{1,13}$	0·4877	$q_{1,13}$	0·1545
$P_{5,12}$	0·5658	$q_{5,12}$	0·1960
$P_{5,14}$	0·6429	$q_{5,14}$	0·2381
P_{67}	0·5986	q_{67}	0·2138
P_{78}	0·4611	q_{78}	0·1455
$P_{13,14}$	0·4841	$q_{13,14}$	0·1582

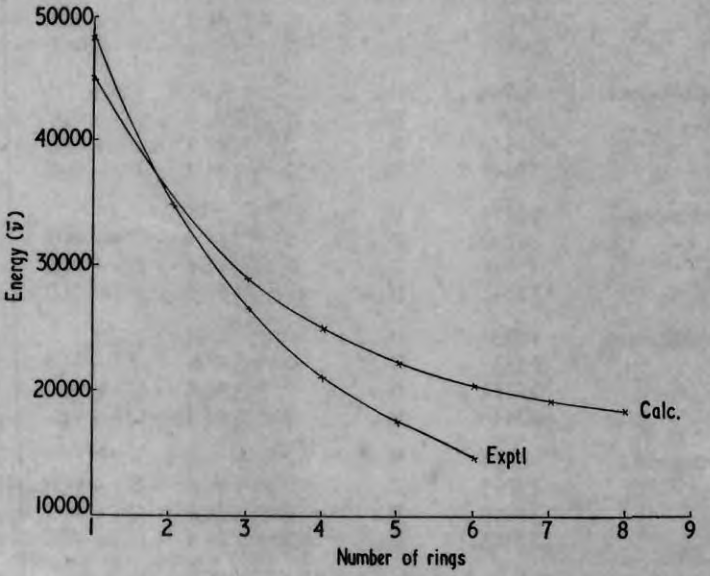

Figure 2. p band for the polyacenes.

Table 3. Energies, symmetries and wave functions for the first four singlet excited states of some polyacenes

	Energy ($\bar{\nu}$)	Symmetry	Wave function
Benzene	39563	B_{3u}	$2^{-1/2}[\Phi(B \rightarrow A') + \Phi(A \rightarrow B')]$
	44704	B_{2u}	$2^{-1/2}[\Phi(A \rightarrow A') - \Phi(B \rightarrow B')]$
	57197	B_{3u}	$2^{-1/2}[\Phi(B \rightarrow A') - \Phi(A \rightarrow B')]$
	57197	B_{2u}	$2^{-1/2}[\Phi(A \rightarrow A') + \Phi(B \rightarrow B')]$
Naphthalene	35448	B_{3u}	$2^{-1/2}[\Phi(B \rightarrow A') - \Phi(A \rightarrow B')]$
	35449	B_{2u}	$\Phi(A \rightarrow A')$
	47972	B_{1g}	$2^{-1/2}[\Phi(C \rightarrow A') + \Phi(A \rightarrow C')]$
	50224	B_{3u}	$2^{-1/2}[\Phi(B \rightarrow A') + \Phi(A \rightarrow B')]$
Anthracene	28738	B_{2u}	$\Phi(A \rightarrow A')$
	33147	B_{3u}	$2^{-1/2}[\Phi(A \rightarrow B') - \Phi(B \rightarrow A')]$
	38712	B_{1g}	$2^{-1/2}[\Phi(C \rightarrow A') + \Phi(A \rightarrow C')]$
	43877	B_{1g}	$2^{-1/2}[\Phi(C \rightarrow A') - \Phi(A \rightarrow C')]$
Naphthacene	24822	B_{2u}	$\Phi(A \rightarrow A')$
	32440	B_{3u}	$2^{-1/2}[\Phi(C \rightarrow A') - \Phi(A \rightarrow C')]$
	33112	B_{1g}	$2^{-1/2}[\Phi(A \rightarrow B') - \Phi(B \rightarrow A')]$
	38858	B_{1g}	$2^{-1/2}[\Phi(A \rightarrow B') + \Phi(B \rightarrow A')]$
Pentacene	22146	B_{2u}	$\Phi(A \rightarrow A')$
	29154	B_{1g}	$2^{-1/2}[\Phi(B \rightarrow A') + \Phi(A \rightarrow B')]$
	32303	B_{3u}	$2^{-1/2}[\Phi(C \rightarrow A') - \Phi(A \rightarrow C')]$
	35047	B_{1g}	$2^{-1/2}(\Phi(B \rightarrow A') - \Phi(A \rightarrow B')]$

For the significance of symbols A, B, ... A', B' ... see footnote to table 1.

Table 4. Energies, symmetries and wave functions for the first four triplet excited states of some polyacenes

	Energy ($\bar{\nu}$)	Symmetry	Wave function
Benzene	25892	B_{2u}	$2^{-1/2}[\Phi(A \rightarrow A') - \Phi(B \rightarrow B')]$
	34804	B_{3u}	$2^{-1/2}[\Phi(A \rightarrow B') - \Phi(B \rightarrow A')]$
	34804	B_{2u}	$2^{-1/2}[\Phi(A \rightarrow A') + \Phi(B \rightarrow B')]$
	39563	B_{3u}	$2^{-1/2}[\Phi(A \rightarrow B') + \Phi(B \rightarrow A')]$
Naphthalene	20698	B_{2u}	$\Phi(A \rightarrow A')$
	30747	B_{1g}	$2^{-1/2}[\Phi(A \rightarrow C') + \Phi(C \rightarrow A')]$
	32635	B_{3u}	$2^{-1/2}[\Phi(A \rightarrow B') + \Phi(B \rightarrow A')]$
	35448	B_{3u}	$2^{-1/2}[\Phi(A \rightarrow B') - \Phi(B \rightarrow A')]$
Anthracene	14394	B_{2u}	$\Phi(A \rightarrow A')$
	26740	B_{1g}	$2^{-1/2}[\Phi(A \rightarrow C') + \Phi(C \rightarrow A')]$
	31409	B_{3u}	$2^{-1/2}[\Phi(A \rightarrow B') + \Phi(B \rightarrow A')]$
	33147	B_{3u}	$2^{-1/2}[\Phi(A \rightarrow B') - \Phi(B \rightarrow A')]$
Naphthacene	10755	B_{2u}	$\Phi(A \rightarrow A')$
	21533	B_{1g}	$2^{-1/2}[\Phi(B \rightarrow A') - \Phi(A \rightarrow B')]$
	31211	B_{3u}	$2^{-1/2}[\Phi(A \rightarrow C') + \Phi(C \rightarrow A')]$
	32440	B_{3u}	$2^{-1/2}[\Phi(A \rightarrow C') - \Phi(C \rightarrow A')]$
Pentacene	8311	B_{2u}	$\Phi(A \rightarrow A')$
	17795	B_{1g}	$2^{-1/2}[\Phi(A \rightarrow B') + \Phi(B \rightarrow A')]$
	31440	B_{3u}	$2^{-1/2}[\Phi(A \rightarrow C') + \Phi(C \rightarrow A')]$
	32303	B_{3u}	$2^{-1/2}[\Phi(A \rightarrow C') - \Phi(C \rightarrow A')]$

$\Phi(B \rightarrow C')$ is the configuration in which one electron has been excited from molecular orbital B to molecular orbital C'.

The energies and the excited state wave functions for the lowest four singlets are given in table 3 and for the triplets in table 4.

In figure 2, we have plotted the energy of the p band (predominantly $\Phi(A \rightarrow A')$) as a function of the number of rings in the molecule. Finally, the oscillator strengths of the singlet transitions are given in table 5.

Table 5. Oscillator strengths for the four lowest transitions of some polyacenes

Benzene	Naphthalene	Anthracene	Naphthacene	Pentacene
0·000	0·000	0·371 (0·1)	0·442 (0·08)	0·497
0·000 (0·100)	0·207 (0·18)	0·000	0·000	0·000
1·199	0·000	0·000	0·000	0·000
1·201	2·162	0·000	0·000	0·000

Experimental values are given in parentheses for the p band (from Jaffe and Orchin 1962).

4. Discussion

Some years ago Pariser published a paper on the polyacenes (Pariser 1956) in which he calculated excited states, bond orders and other properties using Hückel orbitals and configuration interaction with all twenty-five configurations which arise from single electron promotions. He compared his bond orders with those obtained by Pople (1953) for naphthalene. Although the two calculations are in excellent qualitative agreement there are significant quantitative variations. Pariser in his paper states: "He (Pople) has used different numerical values for the integrals and rather than invoking configuration interaction, has calculated the self-consistent fields m.o.'s for the ground state. His results place the bonds in their correct order. Whether this comes about through the application of self-consistent m.o.'s or as a result of different integral values is not clear at present". In table 6 we list the bond orders calculated in (i) the Hückel approximation, (ii) Pople's work, (iii) in Pariser's paper, and finally (iv) in our work. We have used the same integral values as Pariser. Our bond orders are almost identical with those of Pariser. The differences between Pariser's values and Pople's values are due entirely to the use of different integral values. One other point to notice is that in naphthalene inclusion of all singly excited configurations give bond orders identical with the self-consistent bond orders. This points to the equivalence of the one-determinant self-consistent field solution and the many-determinant approximation in which all singly excited states are included in describing the ground state.

Table 6. Comparison of bond orders for naphthalene obtained from different methods

Bond	12	9, 10	23	19
Hückel	0·7246	0·5182	0·6032	0·5547
Pople	0·78	0·60	0·54	0·50
Pariser	0·7434	0·5488	0·5867	0·5353
This paper	0·7453	0·5488	0·5832	0·5352

We pass now to a consideration of the excited states. From figure 2 we see that the theoretical curve of the $\Phi(A \rightarrow A')$ transitions with number of rings approaches a limit which is about 18 000 $\bar{\nu}$. The experimental curve showing the experimental values for the p transition for the first six members of the series does not clearly point to any convergence limit, although extrapolation suggests a possible limit at about 10 000 $\bar{\nu}$ (see figure 2).

Pariser has calculated the excited states for the first five members of the series using extensive configuration interaction. His values are in agreement with ours for all of the states which we have calculated. It is important, however, to make some further detailed comparisons. Pariser's treatment is most complete for naphthalene, in which he has included all configurations which arise from single electron excitations from the π orbitals. In table 7 we give his values for the naphthalene states and their oscillator strengths. It can be seen from table 7 that there is agreement between our values and those obtained by Pariser. It appears that self-consistent field orbitals plus limited configuration interaction give equivalent results to those obtained using Hückel orbitals and extensive configuration interaction. One advantage of our method is that our configuration interaction matrix is simpler than when Hückel orbitals are used. There are no elements between either the ground state and singly excited configurations, or between excited configurations which differ only in the assignment of one electron. The agreement between calculated transition energies derived from self-consistent field orbitals and a set of Hückel orbitals was discussed by McWeeny (1957).

Table 7. Comparision between Pariser's work and our work for naphthalene

	Pariser		This work	
States	Energy	*f* value	Energy	*f* value
A_{1g}	46193	0·000	51671	0·000
	57970	0·000	62438	0·000
B_{1g}	44403	0·000	47972	0·000
	48257	0·000	50801	0·000
B_{2u}	36227	0·256	35449	0·208
	50869	0·699	52897	0·612
	65568	0·851	66661	1·064
B_{3u}	32397	0·000	35448	0·000
	47886	0·000	50224	0·000

Pariser in his paper poses the question: "to what extent should configuration interaction be included, and what is the effect of changing the nature of the m.o.'s?". From our experience here and from the experience of one of us with a series of nitrogen heterocyclic molecules (McWeeny and Peacock 1957, Peacock 1958, Ph.D. Thesis, University of Durham) we can suggest a possible answer to this question. Extensive configuration interaction is difficult to include because of the prohibition size of the resultant problem. On the other hand, even using self-consistent field orbitals, the one-determinant approximation is inadequate to describe the excited states. A compromise seems to offer the best solution. Use of self-consistent field orbitals as the basis of a limited configuration interaction calculation leads to considerable simplification of the matrix elements. We can then use fewer configurations and obtain agreement with the results of a much larger configuration interaction calculation.

In comparing the calculated oscillator strengths with experiment (table 7) we see that our values are much too high. Almost identical values were obtained by Pariser. Like Pariser, we are unable to offer any reason for the discrepancy.

5. Conclusion

It is seen that the lowest absorption bands in the polyacenes tend to a convergence limit. Experimental confirmation of this must await the preparation of the higher members of the polyacene series. Further, it is shown that calculations of spectra using self-consistent field orbitals and limited configuration interaction give results in agreement with those obtained from an extensive configuration interaction calculation using 'crude' orbitals.

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References

JAFFE, H. H., and ORCHIN, M., 1962, *Theory and Applications of Ultraviolet Spectroscopy* (New York: John Wiley), p. 301.

LÖWDIN, P. O., 1950, *J. Chem. Phys.*, **18**, 365.

MCWEENY, R., 1955, *Proc. Roy. Soc.* A, **227**, 288.

—— 1956, *Proc. Roy. Soc.* A, **237**, 355.

—— 1957, *Proc. Phys. Soc.* A, **70**, 593.

MCWEENY, R., and PEACOCK, T. E., 1957, *Proc. Phys. Soc.* A, **70**, 41.

PARISER, R., 1956, *J. Chem. Phys.*, **24**, 250.

PARISER, R., and PARR, R. G., 1953, *J. Chem. Phys.*, **21**, 466, 767.

PEACOCK, T. E., 1959, *J. Chem. Soc.*, 3241.

POPLE, J. A., 1953, *Trans. Faraday Soc.*, **49**, 1375.

—— 1955, *Proc. Phys. Soc.* A, **68**, 81.