

Ab initio Study of the Cyclohexadienyl Anion

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Ab initio calculations have been performed on the cyclohexadienyl anion using various split-valence basis sets. The best energy is obtained using a more diffuse set than the usual 4-31G one. The wavefunction is analysed using both Mulliken population analyses and a method, based on projection operators, due to Roby. These analyses indicate that the greatest portion of the anionic charge is located in the *para*-position, which is in agreement with previous semiempirical predictions.

UNTIL recently there has been little work published on *ab initio* calculations of the electronic structures and properties of organic anions. Indeed, there has been some doubt whether Hartree-Fock theory was appropriate for such systems. However, it is now clear that an adequate picture of the electrons' behaviour in such species may be obtained using reasonably small basis sets. In particular, the so-called 4-31G set of Pople *et al.*¹ has recently been shown by, among others, Streitwieser *et al.*² and by Radom³ to give acceptable results for a number of simple organic anions. A review of this field has recently appeared.⁴

We have a longstanding interest in the cyclohexadienyl anion (Figure 1), arising from our work on

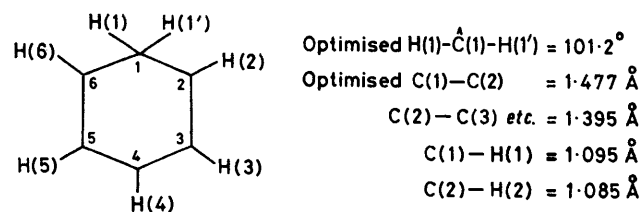


FIGURE 1 Cyclohexadienyl anion, showing numbering used and the partially optimised geometry

nucleophilic aromatic substitutions,⁵ where this anion occupies the same central position in the theory as does the corresponding cation in that of electrophilic aromatic substitution. Some time ago one of us rationalised the observed isomer distributions from nucleophilic replacement of fluoride in polyfluoroaromatic compounds,⁶ using an argument which depended heavily upon a postulated greater concentration of anionic charge at C(4) rather than at C(2) or C(6) (Figure 1). (At that time there were only Hückel calculations available, and even these were of the non-iterative type.) Subsequently other effects have been noted, particularly in kinetic data, leading to some doubts as to the breadth of applicability of this '1 π repulsion' theory: in particular it has been proposed that a fluorine *meta* to the point of attack has a directly beneficial effect upon the ease of formation of the anion produced (*vis-a-vis* one with no fluorine in *meta*-positions).⁷ It is therefore timely that we report here the results of a study of the electronic structure of this anion and of the charge distributions within it.

METHODS

All the LCAO-SCF calculations reported here were performed using the POLYATOM⁸ suite of programs, mounted on the CDC 7600 computers at UMRCC. The geometry of C(2)-C(6) and H(3)-H(7) (Figure 1) was assumed to remain fixed at that for benzene. The H(1)C(1)H(1') angle and the C(1)-C(2) bondlength were optimised in preliminary calculations using the 3G basis set of Stewart⁹ with the modification that it was contracted 2.1 in the valence shells for both C and H. This was done in an attempt to allow for some electronic rearrangement on going to the anion from the neutral species for which the basis set was designed.

A series of calculations were then performed at the calculated optimum geometry. In this series the scale factors used with the 4-31G set were varied systematically, to check on the applicability of the optimum values originally given. Calculations were performed both with the same scale factors for all C and all H atoms, and with scale factors on C(1), H(1), and H(1') which differed from those on C(2)-C(6) and H(2)-H(6). Further calculations were then performed using the best scale factors so found, with the addition of a polarisation set of functions (*s* + *p* + *d*) located at the centre of the regular hexagonal part of the framework. The exponents of these polarisation functions were also varied. Results of selected calculations are shown in Table 1.

Population analyses were carried out for interesting cases, using Mulliken's method and following a more recent suggestion by Roby,¹⁰ which we discuss here.

Projection Density Population Analysis.—A Mulliken population analysis is commonly used to interpret a Hartree-Fock molecular wavefunction in terms of quantities which refer to atoms and bonds, *e.g.* atomic charge and overlap population. However, this method has several disadvantages, such as the dependence of the calculated populations on the basis set used.¹¹ Most of the problems of the Mulliken method are overcome by an alternative approach, due to Roby,¹⁰ which is based on the concept of projection. Projection operators can be set up representing subspaces (for example atomic orbitals, atoms, and pairs of atoms) of the molecular one-electron space and the probability of occupancy of those subspaces calculated. From the resulting occupation numbers, 'overlap populations', and 'atomic charges' may be defined. Since the extended basis sets used to calculate accurate densities generally have no physical meaning, a set of atomic orbitals, $|\mu\rangle$, is constructed from these and the molecular wavefunction is analysed in terms of these atomic orbitals.

TABLE 1

Selected calculations, illustrating the results obtained by varying the scale factors used

Number	Scale factors		Polarisation set coefficients			Total energy	ϵ_{22}
	H	C	<i>s</i>	<i>p</i>	<i>d</i>		
1	1.0	1.0				-230.8222	+0.0081
2	1.0	0.95				-230.8241	+0.0092
3	1.0, ^a 0.95 ^b	0.95				-230.8248	+0.0081
4	0.95	0.95				-230.8243	+0.0081
5	0.95	0.95	0.08	0.06	0.009	-230.8288	+0.0050
6	0.95	0.90	0.08	0.06	0.009	-230.8211	+0.0045
7	0.95	0.95	0.7	0.9	0.95	-230.8288	+0.0085
8	0.95	0.95	0.5	0.7	0.5	-230.8305	+0.0089

^a On H(1) and H(2). ^b On H(3)—H(7).

TABLE 2

Energy quantities and symmetries of filled orbitals in benzene and cyclohexadienyl anion

Benzene		Cyclohexadienyl anion			
		'4-31G' ^a		'4-31G' + polarisation ^b	
Total energy	-230.3590	-230.8222		-230.8305	
Kinetic energy (<i>T</i>)	230.1365	231.44165		230.922 21	
Virial ratio	-2.000 96	-1.997 32		-1.9996	
Orbital	Energy	Symmetry	Energy	Symmetry	Energy
22		$1e_{2u}$ ($2a_2, 3b_1$)	+0.0081	$3b_1$	+0.0085
{21	-0.3401	$1e_{1g}$ ($1a_2, 2b_1$)	-0.1394	$1a_2$	-0.1388
{20			-0.2367	$2b_1$	-0.2361
{19	-0.4931	$3e_{2g}$ ($11a_1, 7b_2$)	-0.2491	$7b_2$	-0.2485
{18			-0.2759	$11a_1$	-0.2753
17	-0.5062	$1a_{2u}$ ($1b_1$)	-0.3551	$10a_1$	-0.3539
{16	-0.5924	$3e_{1u}$ ($10a_1, 6b_2$)	-0.3642	$6b_2$	-0.3628
{15			-0.3772	$1b_1$	-0.3768
14	-0.6247	$1b_{2u}$ ($5b_2$)	-0.3877	$5b_2$	-0.3870
13	-0.6408	$2b_{1u}$ ($9a_1$)	-0.4333	$9a_1$	-0.4330
12	-0.7140	$3a_{1g}$ ($8a_1$)	-0.4908	$8a_1$	-0.4905
{11	-0.8267	$2e_{2g}$ ($4b_2, 7a_1$)	-0.5947	$4b_2$	-0.5941
{10			-0.6222	$7a_1$	-0.6216
{9	-1.0203	$2e_{1u}$ ($3b_2, 6a_1$)	-0.7878	$3b_2$	-0.7867
{8			-0.8000	$6a_1$	-0.7990
7	-1.1593	$2a_{1g}$ ($5a_1$)	-0.9170	$5a_1$	-0.9161
6	-11.2281	$1b_{1u}$ ($4a_1$)	-10.9566	$4a_1$	-10.9559
{5	-11.2284	$1e_{2g}$ ($3a_1, 2b_2$)	-10.9798	$2b_2$	-10.9791
{4			-10.9798	$3a_1$	-10.9791
{3	-11.2292	$1e_{1u}$ ($2a_1, 1b_2$)	-11.0141	$2a_1$	-11.0136
{2			-11.0237	$1b_1$	-11.0231
1	-11.2295	$1a_{1g}$ ($1a_1$)	-11.0237	$1a_2$	-11.0231

^a Scale factors used for C, 0.95; for H, 0.95. ^b See Table 1.

The occupation numbers (η_A) give a measure of the maximum number of electrons which can be associated with an atomic orbital, atom, pair of atoms, *etc.*; *i.e.* they include that electron density shared with other atomic orbitals not in the group being considered. The occupation number of an atom will generally lie between the number of electrons associated with the isolated neutral atom, N_A , and the maximum possible value when all the atomic orbitals on the atom have an occupation number of two. This leads to a definition of the 'charge' on an atom as in equation (1).

$$q_A = N_A - \eta_A \quad (1)$$

The charge will generally be negative because of the shared electron density included in η_A .

DISCUSSION

The best gauge of the accuracy of any theoretical results is comparison with experiment; however, there seems to be no experimental result available for comparison here. It may be however that ion cyclotron resonance spectroscopy and/or negative ion mass spectroscopy will soon develop to the point where H^- is easily

* 1 cal = 4.184 J; 1 Hartree = 2 625.46 kJ.

available and will therefore provide results for comparison. We have estimated the energy of formation of the cyclohexadienyl anion from benzene and H^- , using calculations for benzene and H^- in 4-31G bases. Of course, we can make no allowance for correlation energy and so our results are indicative only. Our estimate of this energy is 6.7 kcal * from the best 4-31G calculation, or 11.8 kcal using the 4-31G + polarisation calculation. The former is a fairer estimate, since the benzene calculation is without polarization. This very small value contrasts sharply with the heat of protonation of benzene,¹² which is *ca.* 180—185 kcal mol⁻¹ and because of the limited basis set used, casts some doubt on the actual stability of the molecule, particularly since the H^- calculation (with scale factor of 0.96) gave a virial ratio (V/T) of -1.788, suggesting that exponents could be considerably improved. Such improvement would of course reduce the calculated binding energy of the cyclohexadienyl anion with respect to benzene plus H^- . Thus, we predict that the species will be only weakly bound, if it is stable at all.

In Table 2 we show the values of various quantities, and of the orbital energies we calculate for the 'best' 4-31G basis and for our 'best' calculation using the polarisation set. We also show orbital energies for benzene in the standard 4-31G basis. We have labelled the orbitals with their symmetries; in the case of benzene we give both the C_{2v} and D_{6h} labels.

As expected, in the anion all the energy levels are displaced from their positions in benzene towards higher energies and we note that this displacement is substantial even for the inner, non-valence electrons in the carbon 1s orbitals; in fact all the orbitals are shifted by *ca.* 0.2 Hartree with only fairly small deviations from this value. This corresponds well with the results quoted by Ermler *et al.*,¹³ where the orbitals in the benzenonium (cyclohexadienyl) cation were found to be *ca.* 0.2 Hartree *more* stable than the corresponding benzene orbitals.

molecular centre gave a significant improvement in the total energy, but did not show any marked improvement in the value of ϵ_{22} .

Of course, the unbound nature of this orbital is not a real difficulty in solution, where solvation effects, the proximity of the gegenion, *etc.*, will all act to stabilise the outermost electrons. Also, a complete geometry optimisation, or larger basis set, might well give bound states for all the electrons.

We have a particular interest in the distribution of charge in the molecule, since it is on this that substituents will act, and we have carried out Mulliken population analyses on several of our calculated wavefunctions. We display in Table 3 the results of such analyses obtained from the original basis set of Pople *et al.* (standard 4-31G), that from our best unpolarised calculation ('best' 4-31G) and that for the best (*i.e.* best total energy) polarisation basis set (4-31G +

TABLE 3
Mulliken analyses of selected wavefunctions

	Standard 4-31G			Best 4-31G			4-31G + polarisation		
	Total electrons		Total (nett charge)	Total electrons		Total (nett charge)	Total electrons		Total (nett charge)
	σ	π		σ	π		σ	π	
C(1)	5.275	1.028	-0.303	5.122	0.954	-0.076	5.168	0.945	-0.114
C(2)	5.045	1.312	-0.357	4.979	1.318	-0.297	4.984	1.289	-0.272
C(3)	5.208	0.948	-0.156	5.071	0.954	-0.025	5.109	0.946	-0.055
C(4)	4.99	1.43	-0.423	4.893	1.424	-0.317	4.871	1.432	-0.303
H(1)	0.386	0.512	0.102	0.437	0.540	+0.023	0.437	0.540	+0.023
H(2)			0.094			-0.007			0.0
H(3)			0.132			+0.013			+0.026
H(4)			0.094			-0.019			-0.013
C(1)-C(2)	0.182	0.134	0.616	0.660	-0.044	0.616	0.637	-0.058	0.579
C(2)-C(3)	0.689	0.432	1.121	0.616	0.503	1.119	0.721	0.428	1.150
C(3)-C(4)	0.671	0.178	0.849	0.612	0.176	0.788	0.640	0.169	0.809
C(1)-H(1)	0.400	0.408	0.808	0.338	0.398	0.776	0.368	0.404	0.772
C(2)-H(2)			0.822			0.781			0.764
C(3)-H(3)			0.810			0.802			0.774
C(4)-H(4)			0.826			0.812			0.792

An important feature of the eigenvalues presented for the 'best' 4-31G calculation on the ion in Table 2 is that the highest occupied orbital, ϵ_{22} , is unbound, as is not uncommon in calculations on anions, particularly in cases where the geometry is only partially optimised. We have not carried out extensive calculations, involving *d* functions on carbon and *p* functions on hydrogen, for this molecule, but it seems clear that electrons in the HOMO will be at best only weakly bound, and might thus be best represented as being in a Rydberg state. The large values of the coefficients of the outermost components, in the 4-31G basis, calculated for the highest filled orbital also lent credence to this. For this reason calculations have been made including a set of (*s* + *p* + *d*) functions at the 'centre' of the molecule, in an attempt to investigate this possibility.

The results of these calculations may be summed up by saying that they gave disparate results: use of very diffuse functions did lower ϵ_{22} , albeit never to negative values, but the overall total energy calculated became worse. Use of relatively non-diffuse functions at the

polarisation) calculation. Some discussion of the results is required here. We point out again that the geometry is only partially optimised, so that the results must be interpreted with care.

If we consider first the effect of changes in basis set upon the electron distribution, then it is noteworthy that the standard 4-31G set predicts that there will be a high concentration of charge on all the carbon atoms, with substantial negative charge on C(1), *as well as* on C(2)[C(6)] and C(4), whereas both the other calculations show smaller charges on the carbons. The most noticeable change is on C(1) but the effect on the other carbons is also substantial. The two more diffuse bases place correspondingly more charge on the hydrogen atoms. Interestingly, the polarisation set does not carry this process as far as does the best 4-31G, although the difference here is small.

Turning now to the π and quasi- π (orbitals 15 and 20-22) populations, we note here the fairly small re-arrangement of charge in the CH_2 group, and in electron populations generally, on changing bases. [Of course,

in these basis sets there can be no π charge on H(2)–H(7).] The most noticeable change is in the π bond orders for C(1)–C(2) and C(2)–C(3), where use of the more diffuse set increases the C(2)–C(3) bond order at the expense of C(1)–C(2). There is an accompanying (small) rearrangement of charge in the CH₂ group, with some charge moving from C to H. It is noteworthy, also, that the eigenvectors for ϵ_{22} show that this orbital is

The analysis of the standard 4-31G calculation by Roby's method,¹⁰ which is known to be much less basis-set-dependent than the Mulliken procedure, is shown in Table 4.

The results here require some amplification, and we emphasise again that the quantity of charge associated with an atom by this calculation has *not* the same meaning as has a Mulliken charge, but rather represents

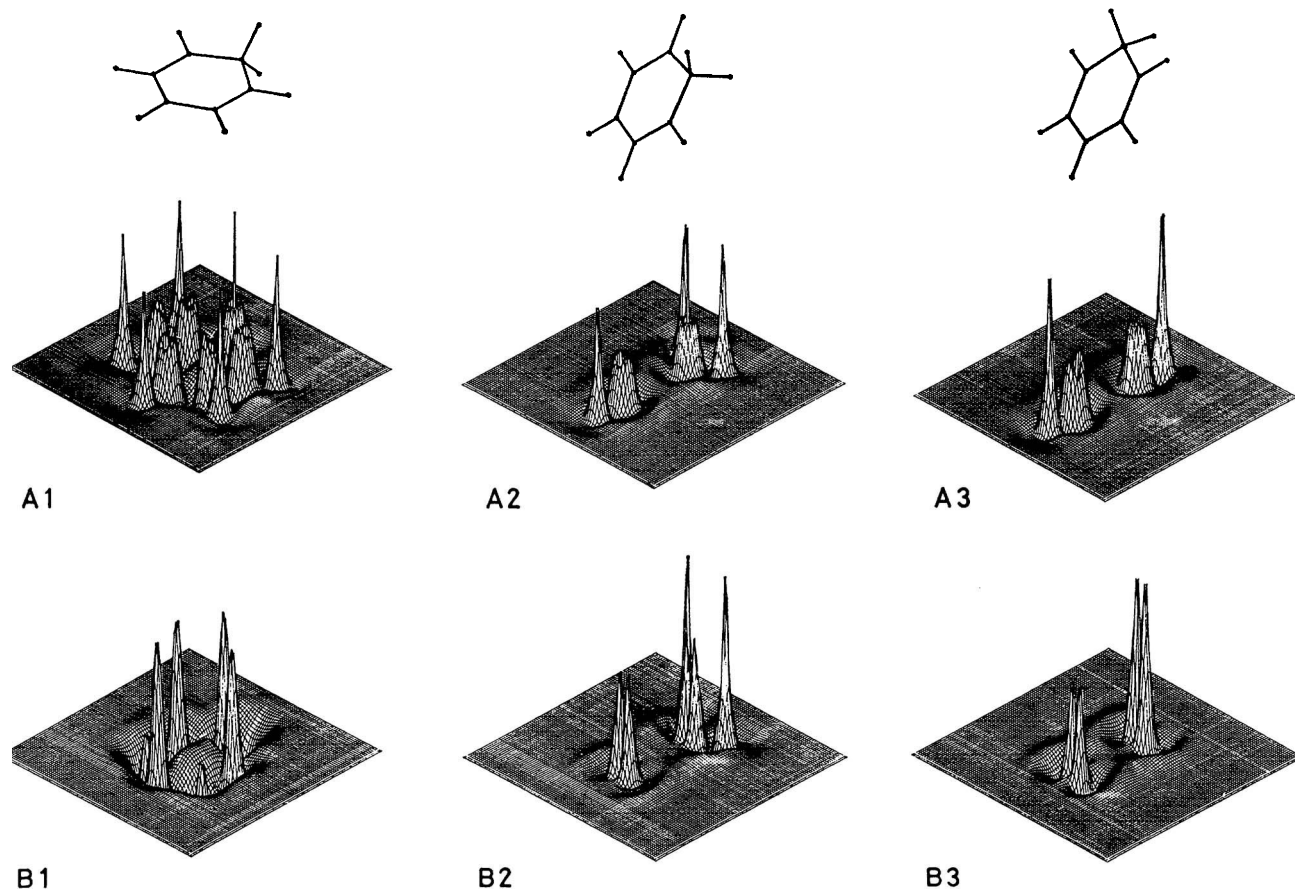


FIGURE 2 Electron-density difference maps for C₆H₇⁻ in three planes. All maps: standard 4-31G values – best 4-31G values. Planes: A₁, in molecular plane; A₂ through H(1), H(2), C(1), C(4); A₃ normal to A₁, through C(2), C(5); B₁ parallel to A₁, but raised 0.8 Bohr (1 Bohr = 5.29167 × 10⁻¹⁰m); B₂, B₃ as A₂, A₃. A, total electron density difference, B, π electron-density difference. Greatest values (electron/Bohr³) plotted: A₁, 1.73 × 10⁻²; A₂, 1.73 × 10⁻²; A₃, 1.44 × 10⁻²; B₁, 1.42 × 10⁻³; B₂, 8.35 × 10⁻³; B₃, 4.71 × 10⁻³.

made up mostly from the outermost components of the 4-31G basis set in each case.

The corresponding σ populations show, again, a variation with basis set, and again the difference is most noticeable in the C(1)H(1)H(1') grouping. However, the significance of these and other variations between the populations calculated for the three wavefunctions is questionable because of the known¹¹ basis-set-dependence of the Mulliken analysis. The calculated energies are in fact very similar and electron-density difference maps (Figure 2) show that the actual variations in the electron densities are very small. Of course, there is nothing to say that the charge will vary most in the planes we show, but they are a number of slices through the molecule, and should be representative.

the degree to which the atom has succeeded in 'completing its octet' in the old-fashioned sense. Thus, the maximum population to be expected on H will be 2.0

TABLE 4
Projection operator analysis¹⁰ of the standard 4-31G wavefunction

Atomic populations			Overlap populations		
	Total	π		Total	π
H(1)	1.667		C(1)–H(1)	1.362	
H(2)	1.688		C(2)–H(2)	1.417	
H(3)	1.667		C(3)–H(3)	1.421	
H(4)	1.693		C(4)–H(4)	1.426	
C(1)	9.009	1.727	C(1)–C(2)	1.539	0.095
C(2)	8.844	1.578	C(2)–C(3)	1.002	0.454
C(3)	8.741	1.380	C(3)–C(4)	1.834	0.299
C(4)	8.987	1.703			

and the maximum on C will be 10.0 electrons, corresponding in each case to wholly filled valence shells. This obviously makes difficult a simple interpretation of the results in terms of fractional charges, *etc.*, but it is clear that atoms with larger populations associated with them will be more electron-rich than those with smaller. The interpretation of overlaps is more straightforward, since it corresponds closely with the common organic chemists' idea of two electrons per bond (and minus two electrons per antibond).

With these observations made, we comment that here the total population is largest on C(1), as might be expected since this, unlike C(2)-C(4), is bonded to four other atoms. The difference in the latter three values are in the expected (from the earlier results and from our Mulliken analyses) directions, so that C(4) is appreciably more negative than C(2), which is much more electron-rich than is C(3). The populations on the hydrogen atoms are all very similar.

The total overlap populations again confirm the general trend of the Mulliken analyses with, amongst the C-C bonds, the C(2)-C(3) bond being the strongest, closely followed by C(3)-C(4), and with C(1)-C(2) being considerably weaker. Interestingly, the separation of these overlaps into σ and π contributions shows that the bulk of these differences must be ascribed to π bonding effects, since the σ bonds are of very comparable strengths [particularly C(2)-C(3) and C(3)-C(4)]. A similar dissection of the atomic-charge populations yields the corresponding result, that the σ atomic populations (on carbon) are very similar with C(3) a narrow winner, a result which may prove important in subsequent studies on aromatic substitution, so that here, again, the differences in total populations are closely ascribable to π effects.

We thus, finally, arrive at the conclusion that the traditional picture, with π effects superimposed upon a

comparatively undifferentiated framework of C-C σ bonds, is still a reasonable way of looking at conjugated molecules. Of course, this cannot be taken too far, but it is noteworthy that calculations such as the present ones, using a split valence level basis set and the full *ab initio* formalism, yield a final picture not very different from the semi-intuitive ones in use for many years. We also note that this work supports the idea, basic to the 1π repulsion theory of nucleophilic aromatic substitution in fluoroaromatics, that the π charge is greatest on C(4).

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