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FULVALENE IONS—I

CALCULATIONS ON CALICENE IONS

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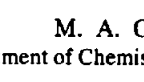
Abstract—Calculations on planar and 90°-twisted calicene and the mono- and di-ions derived from it are reported. Both all-valence-electron and π-electron calculations were performed, utilizing an "all aromatic" geometry throughout. Calculated ionization energies indicate that there should be no appreciable gain in resonance stabilization upon radical formation, however the radicals should be amenable to preparation. Good general agreement was obtained between the π-electron charge and spin distributions predicted by the INDO and PPP methods. In addition, these are generally in good agreement with simple predictions based on Hückel's (4n + 2) rule.

INTRODUCTION

Calicene (triapentafulvalene, 1), though still an unknown compound, has been the subject of a number of investigations. The early Hückel molecular-orbital (HMO) calculations of Roberts *et al.*[1] attributed a high degree of aromaticity to the compound on the basis of the calculated delocalization energy. The large dipole moments found for several calicene derivatives[2] appeared to be consistent with large contributions from "aromatic" resonance structures in which both rings attain Hückel's number of (4n + 2) π-electrons (i.e., the three-membered ring positive and the five-membered ring negative).



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Later calculations, however, indicated that calicene should be considered to be polyolefinic rather than aromatic. The improved Hückel-type calculations of Nakajima *et al.*,[3] in which the effect of sigma-bond compressions were taken into account, predicted a degree of bond alternation in calicene comparable to that found in butadiene. Moreover, these authors calculated the diamagnetic anisotropy and the free valence reactivity indices, and concluded from the results that there is no basis for ascribing aromatic character to calicene. It is interesting that, in spite of these results, the π-charge densities were still found to be fairly uniform in each of the rings. The 3-membered (C_3) ring was found to be positive and the 5-membered (C_5) ring negative, the charge separation being sufficient to predict a dipole moment of 5·70 D.

Approximate self-consistent field (SCF) calculations both of the π-electron[4] and the all-valence-electron variety[5] tend to substantiate the conclusions of Nakajima *et al.* Dewar and Kohn[5] predicted even greater bond alternation than that found by Nakajima *et al.* In addition, the calculated total formal atomic charges present a very different picture from the π-charge densities. A large dipole moment was still predicted, and in the same direction as before, but the separated charge was strongly concentrated on carbons 7 and 8 which form the inter-ring bond.

The question of aromaticity of calicene is not yet closed, however. Hess and Schaad[6,7] have recently revived interest and faith in the HMO theory by showing that it is capable of predicting resonance energy as accurately as Dewar's SCF calculations. Their latest results,[7] which include estimates of sigma effects, predict almost as much total resonance energy for calicene as for benzene. Moreover, they point out that this is consistent with experiment in that simple derivatives of calicene have been prepared; they appear to have high stabilities, and are known to undergo electrophilic substitution reactions.[8]

While the question of calicene's aromaticity is still open, we wish to direct attention to the fact that pertinent information should be available from a study of calicene's positive and negative ions along with the neutral molecule. Addition or removal of an electron from calicene provides the possibility of aromatic resonance structures without the prerequisite of charge separation that exists in the neutral molecule. Thus one expects that the degree of aromaticity should be enhanced in the mono-ions. Moreover, since the mono-ions are free radicals, electron spin resonance experiments should provide a direct measure of the degree of spin density delocalization. The di-ions, if they can be prepared, will be diamagnetic, and their charge distributions could be probed by nuclear magnetic resonance experiments.

The relative energies, and charge and spin density distributions in calicene's ions are therefore of considerable interest. In this paper, we wish to report the results of some molecular-orbital calculations on these species. Since the barrier to rotation around the central C$_7$—C$_8$ bond is obviously related to the contributions made by the aromatic resonance structures, and it has been discussed previously by several other investigators,[5,9] we have carried out calculations on both the planar and twisted forms of all species ranging from the dication to the dianion.

METHODS

All the calculations reported in this paper were carried out for an "all aromatic" geometry. By this is meant that each ring is a planar regular polygon, and that all C—C bonds are 1·395 Å long. The hydrogens were assumed to lie in the planes of the rings to which they are attached; each C—H bond was assumed to bisect the exterior angle of the ring at the point of attachment with length 1·10 Å.

The all-valence electron calculations were carried out using the INDO approximations of Pople *et al.*[10] Our computer program was a slightly modified version of the one given by Pople and Beveridge in their book.[10] All the parameters used were the ones given by Pople and Beveridge,[10] except that the orbital exponent for the hydrogen 1s orbital was set equal to 1·2. Both open and closed shell Hartree-Fock calculations were carried out with this program. For the anion and cation radicals we also employed the "half-electron method" (1/2e) that was introduced by Dewar *et al.*[11]. These 1/2e calculations were carried out by modifying the Pople-Beveridge program, and retaining the INDO approximations and standard parameter values. Dewar *et al.*[11] reported that the standard unrestricted open-shell calculation overestimates binding energies for free radicals by about 0·5 eV (12 kcal/mole) and that this was corrected by employing the 1/2e method. Although the absolute energies of the molecular binding energies obtained from INDO calculations are not as good as those obtained by Dewar with the MINDO approximations,[11] we have generally found that for free radicals the 1/2e method decreases the calculated binding energy by about the same amount ($\leq$0·5 eV) in the INDO method.

In the next section, when calculated results are quoted, the 1/2e results will be used whenever the energy of a doublet-state species is involved. On the other hand, when discussing charge or spin density distributions for these species, we will use the results of the standard unrestricted Hartree-Fock (UHF) procedure. There were some cases where the UHF and 1/2e methods gave considerably different results for charge and spin densities. This is to be expected, since the 1/2e method is a restricted approximation.

Parallel calculations were also carried out considering only the π-electrons. These were the standard Pariser-Parr-Pople (PPP) calculations.[12] Nearest neighbor resonance integrals were taken as $-2{\cdot}395$ eV; one-center repulsion integrals were set equal to 11·13 eV; two-center repulsion integrals were estimated by the Mataga-Nishimoto approximation;[13] the core potential was evaluated with the procedure of Goeppert-Mayer and Sklar,[14] neglecting neutral penetration integrals; total π-electron energies were calculated using a valence-state-ionization potential of 11·16 eV for C atoms, and including an approximation for the core-repulsion energy based on the two-center repulsion integrals.

ENERGIES

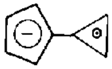
The calculated barriers to rotation for all species are shown in Table 1, along with the C$_7$—C$_8$ π-bond orders for the planar systems. Our INDO result for neutral calicene compares favorably with the 27·0 kcal/mole calculated by Dewar and Kohn,[5] and the PPP calculations agree with the PPP results of Gleicher and Arnold[9].

Table 1. Rotational barriers[a] and π-bonded orders

	Rotational barriers				C$_7$—C$_8$ π-bond orders	
	INDO		PPP		INDO	PPP
Species	eV	kcal/mole	eV	kcal/mole		
○	0·99	22·8	2·28	52·6	0·601	0·656
⊖	0·19	4·4	0·36	8·4	0·428	0·408
⊕	0·32	7·5	1·41	32·5	0·486	0·498
^{1}⊜	0·25	5·6	0·52	11·9	0·530	0·558
^{3}⊜	0·51	11·8	0·52	11·9	0·464	0·558
^{1}⊕⊕	−0·60	−13·9	1·18	27·2	0·404	0·387
^{3}⊕⊕	−0·69	−15·9	1·18	27·2	0·361	0·387

[a] Negative barriers indicate that the twisted form is more stable than the planar form.

The INDO calculations for the mono-ions clearly indicate that the barrier to rotation decreases drastically upon ionization. The PPP results for the anion radical substantiate this result but for some reason indicate a barrier increase for the cation radical. Table 1 also shows that upon ionization the π-bond order for the exocyclic bond decreases appreciably which is consistent with the decrease in barrier height. These results can be rationalized to some extent by structures such as 2 and 3, in which one of the rings is "aromatic" and should indicate a tendency for the two rings to behave independently.



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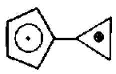

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It is interesting that for the dication the INDO calculations show that the twisted form should be more stable than the planar form for both singlet and triplet multiplicity.

It should perhaps be noted that, of all the results discussed in this paper, the rotational barriers are the quantities which are most likely to be affected when further calculations are carried out to optimize molecular geometries.

Table 2 reports the ionization potentials of all species in both the planar and twisted forms, calculated by two methods; a direct energy difference between the two species involved (ΔE), and according to Koopmans' Theorem[15] (KT). A value of about 8–9 eV as reported for neutral calicene in Table 2 is a reasonable number for a π-IP.[16] This value seems to indicate that the cation radical does not have greater "aromatic character" than the neutral calicene, based on the fact that 8·3 eV is a typical π-IP for non-aromatic C_8 systems. If formation of the cation radical were accompanied by a sizeable increase in resonance energy, this should be reflected by an appreciably smaller value for the π-IP.

The same conclusion is questionable for the anion radical since the results show that neutral calicene may have a positive electron affinity. Even though these results do not show appreciable gains in resonance stabilization for calicene radicals, one should still be able to obtain these species experimentally since counterions and solvent effects should supply additional stabilization. It should be mentioned that other molecules with high ionization potentials have been produced experimentally such as the cyclooctatraene cation radical[17,18] which has an IP of 8·0 eV[17,18,19] which compares to the value of 8·3 eV calculated for the IP of calicene.

Another interesting point is that the INDO calculations predict triplet ground states for the di-ions in both the planar and twisted conformations. For the dianion the lowest triplet state is approximately 2·5 eV (58 kcal/mole) lower than the lowest singlet state, while for the dication the difference is approximately 0·7 eV (16 kcal/mole). For the dication the predicted order of stability is: triplet 90° twisted > triplet planar > singlet 90° twisted > singlet planar, while for the dianion the predicted order of stability is: triplet planar > triplet 90° twisted > singlet planar > singlet 90° twisted.

CHARGE AND SPIN DISTRIBUTION

Tables 3 and 4 show the π-electron densities obtained for all species from the INDO and PPP calculations, respectively. Also listed for each case are the total numbers of π-electrons associated with each ring. For the twisted conformations it must be borne in mind that the INDO technique provides combinations of the π-orbitals of each ring with the σ-orbitals of the other. Clearly, a σ-π separation is not at all justifiable in that case, but we nevertheless find it interesting and convenient to focus temporarily on the π-orbitals of each ring separately.

It is obvious from Tables 3 and 4 that the π-orbital densities obtained from the two methods are in general very close to one another. This is perhaps not too surprising for the planar species, but one might have expected sizeable differences for the twisted forms. Apparently, the number of π-electrons frozen into each ring in the PPP calculations is generally quite close to the number giving the most stable charge distribution when σ-π interaction is permitted in the INDO calculation. This result provides somewhat surprising justification for the treatment of such systems via π-electron methods alone, even for twisted geometries. The

Table 2. Ionization potentials (eV)

	Planar				90° Twisted			
	INDO		PPP		INDO		PPP	
Species	ΔE[a]	KT[b]	ΔE[a]	KT[b]	ΔE[a]	KT[b]	ΔE[a]	KT[b]
^{1}⊜	−6·24	−9·12	−8·66	−3·82	−10·25	8·99	4·53	7·08
⊖·	−2·08	−0·96	2·27	2·48	−1·26	1·22	4·19	4·33
○	8·30	9·19	7·81	8·31	7·64	8·36	6·94	7·93
⊕·	16·01	16·61	14·29	13·20	15·07	15·67	14·06	12·48

[a] Differences in binding energies calculated via UHF method.

[b] Calculated via Koopmans' Theorem.

Table 3. π-Orbital densities calculated by INDO method

	C_5 ring				C_3 ring		
Atom Species	1	2	8	$N_\pi(C_5)^a$	6	7	$N_\pi(C_3)^a$
				Planar forms			
○	1·116	1·090	1·203	5·614	0·808	0·770	2·386
⊕	0·787	0·979	1·237	4·770	0·746	0·720	2·230
⊖	1·232	1·182	1·139	5·965	0·901	1·233	3·035
^{1}⊕⊕	0·397	0·900	1·265	3·858	0·711	0·719	2·141
^{1}⊖⊖	1·413	1·237	1·016	6·315	0·985	1·715	3·685
^{3}⊕⊕	0·775	0·754	0·895	3·951	0·652	0·745	2·049
^{3}⊖⊖	1·291	1·224	1·095	6·124	1·345	1·186	3·876
				Twisted forms			
○	1·183	1·139	1·283	5·926	0·750	0·637	2·137
⊕	1·161	0·900	0·917	5·039	0·725	0·660	2·110
⊖	1·213	1·182	1·198	5·988	1·210	0·663	3·083
^{1}⊕⊕	1·253	0·686	0·499	4·138	0·699	0·685	2·091
^{1}⊖⊖	1·161	1·217	1·094	6·036	1·684	0·692	4·052
^{3}⊕⊕	0·811	0·793	0·882	4·090	0·691	0·691	2·074
^{3}⊖⊖	1·243	1·224	1·081	6·014	1·352	1·284	3·987

^{a} $N_\pi(C_5)$ and $N_\pi(C_3)$ are total numbers of π-electrons in the C_5 and C_3 rings, respectively.

Table 4. π-Orbital densities calculated by PPP method

	C_5 Ring				C_3 Ring		
Atom Species	1	2	8	$N_\pi(C_5)^a$	6	7	$N_\pi(C_3)^a$
				Planar Forms			
○	1·104	1·080	1·141	5·509	0·828	0·836	2·491
⊕	0·837	0·957	1·157	4·745	0·748	0·760	2·255
⊖	1·211	1·200	1·146	5·968	0·927	1·177	3·032
^{1}⊕⊕	0·460	0·890	1·173	3·872	0·681	0·766	2·128
^{1}⊖⊖	1·368	1·276	1·080	6·368	0·985	1·661	3·632
^{3}⊕⊕	0·460	0·890	1·173	3·872	0·681	0·766	2·128
^{3}⊖⊖	1·368	1·276	1·080	6·368	0·985	1·661	3·632
				Twisted Forms			
○	1·179	1·160	1·321	6·000	0·709	0·583	2·000
⊕	1·096	0·903	1·002	5·000	0·669	0·662	2·000
⊖	1·185	1·199	1·233	6·000	1·127	0·746	3·000
^{1}⊕⊕	1·085	0·635	0·561	4·000	0·623	0·753	2·000
^{1}⊖⊖	1·190	1·235	1·151	6·000	1·582	0·836	4·000
^{3}⊕⊕	1·085	0·635	0·561	4·000	0·623	0·753	2·000
^{3}⊖⊖	1·190	1·235	1·151	6·000	1·582	0·836	4·000

^{a} $N_\pi(C_5)$ and $N_\pi(C_3)$ are total numbers of π-electrons in the C_5 and C_3 rings, respectively.

spirit of this finding is certainly similar to the conclusions of Schaad and Hess,[7] who found that (for planar species) resonance energies can be accurately estimated from a π-electron calculation.

The second striking observation from Tables 3 and 4 is that in most cases one ring almost succeeds in obtaining Hückel's number of $(4n+2)$ π-electrons The main exceptions are the planar neutral molecule and the planar singlet dianion. Exceptions in the planar neutral species are expected from simple electrostatic considerations, for large charge separations have to be introduced in order to obtain 6 and 2 π-electrons in the two rings. Twisting the molecule apparently facilitates the process of obtaining aromatic numbers of π-electrons because each ring can draw electrons from or push them into the σ-system of the other ring without causing large charge separations. We must conclude from this that the $(4n+2)$ rule, as exemplified by resonance structures **2** and **3**, does in fact have some predicitive usefulness in describ- in fact have some predictive usefulness in describ- ing charge distributions.

In addition to describing total numbers of π-electrons, resonance structures **2** and **3** imply uniform distributions of the π-electrons in their "aromatic" portions. This too, is approximately borne out in Tables 3 and 4. The 6 π-electrons in the C_5 ring of **2** are nearly uniformly distributed, as are the 2 π-electrons in the C_3 ring of **3**. Furthermore, on going from the mono-ions to the di-ions (of both positive and negative charge) the largest changes in π-electron density occur in the ring which does not contain $(4n+2)$ π-electrons. Once a ring attains Hückel's number of π-electrons, it apparently prefers to retain that number, even when the total molecular charge is changed. This can be seen in Tables 5 and 6.

For various ionization processes involving planar molecules and ions, Table 5 lists: ΔN_π, the change in the number of π-electrons associated with each ring; ΔN_c, the change in the total number of carbon atom valence electrons for each ring; ΔN_{tot}, the change in the total number of electrons associated with each ring, including those on hydrogen atoms. The numbers in parentheses are those derived from the PPP calculations, while all others are from the INDO results. It is clear from these numbers that ΔN_π, from either the PPP or the INDO treatment, generally gives a very good approximation to ΔN_{tot}. Most frequently, the magnitude of ΔN_c is slightly less than ΔN_π, as would be expected from simple electrostatic considerations. But when the hydrogens are included to obtain ΔN_{tot}, that number turns out to be fairly close to ΔN_π for each ring.

Table 6 is the same as Table 5, except that it was constructed by using the charge distribution for the most stable species according to the INDO calculation. The conclusions with regard to the INDO results are similar to those mentioned above, that is, the change in the number of π-electrons in each ring comes close to the change in the total number of electrons. However, in this table the PPP results do not agree as well with the INDO data, especially for the second ionizations listed. We have no ready explanation for this.

The π-electrons do not of course tell the whole story about the charge distributions. For example, the total charge distribution in neutral calicene is such that the calculated dipole moment is 8·10 D, with the C_3 ring positive. The twisted form of neutral calicene has a dipole moment of 10·85 D in the same direction. Both of these are in the same direction indicated by the tendency of the C_5 ring to attain 6 π-electrons. However, while the π-electrons are almost uniformly distributed in each ring, the total charge is not. The carbons forming the exocyclic bond carry the largest charge in both structures. All carbons in the C_3 ring are positively charged, and those in the C_5 ring carry negative charges. In each case every hydrogen atom has the same sign of charge as that of the entire ring to which it is attached. The magnitudes of the hydrogen charges are comparable to or slightly greater than those of the carbon atoms. These are illustrated in Fig 1.

Table 5. Changes in number of electrons associated with each ring for vertical ionization processes, from INDO calculations. (All planar species).[a]

Process		C_5 ring	C_3 ring
	ΔN_π	−0·844 (−0·764)[a]	−0·156 (−0·236)[a]
$\bigcirc \rightarrow \dot{\oplus}$	ΔN_c[b]	−0·479	−0·137
	ΔN_{tot}	−0·776	−0·224
	ΔN_π	+0·351 (+0·459)[a]	+0·649 (+0·541)[a]
$\bigcirc \rightarrow \dot{\ominus}$	ΔN_c[b]	+0·215	+0·412
	ΔN_{tot}	+0·420	+0·580
	ΔN_π	−0·911 (−0·873)[a]	−0·089 (−0·217)[a]
$\dot{\oplus} \rightarrow {}^{1}\overset{+}{\oplus}$	ΔN_c[b]	−0·517	−0·100
	ΔN_{tot}	−0·824	−0·176
	ΔN_π	+0·350 (+0·400)[a]	+0·650 (+0·600)[a]
$\dot{\ominus} \rightarrow {}^{1}⊜$	ΔN_c[b]	+0·216	+0·422
	ΔN_{tot}	+0·276	+0·724

[a] Numbers in parentheses are from PPP calculations.

[b] ΔN_c is the change in the total number of valence electrons associated with carbon atoms.

Table 6. Changes in number of electrons associated with each ring for ionization processes involving the most stable form of each ion (INDO calculations)[a]

Process[c]		C_5 ring	C_3 ring
	ΔN_π	−0·844 (−0·764)[a]	−0·156 (−0·236)[a]
$\bigcirc \rightarrow \dot{\oplus}$	ΔN_c[b]	−0·479	−0·137
P P	ΔN_{tot}	−0·776	−0·224
	ΔN_π	+0·697 (+0·491)[a]	+0·374 (+0·509)[a]
$\bigcirc \rightarrow \dot{\ominus}$	ΔN_c[b]	+0·452	+0·213
P T	ΔN_{tot}	+0·620	+0·380
	ΔN_π	−0·181 (−0·873)[a]	−0·819 (−0·127)[a]
$\oplus \rightarrow {}^{3}\overset{+}{\oplus}$	ΔN_c[b]	−0·148	−0·465
P P	ΔN_{tot}	−0·244	−0·756
	ΔN_π	+0·793 (+0·368)[a]	+0·136 (+0·632)[a]
$\ominus \rightarrow {}^{3}⊜$	ΔN_c[b]	+0·497	+0·141
T P	ΔN_{tot}	+0·684	+0·316

[a] Numbers in parentheses are from PPP calculations.

[b] ΔN_c is the change in the total number of valence electrons associated with carbon atoms.

[c] P denotes planar, T denotes twisted.

Table 7. Carbon atom π-orbital spin densities

	Planar Cation radical		Twisted Cation radical	
Atom	INDO	PPP	INDO	PPP
1	+0·452	+0·542	−0·097	−0·340
2	+0·098	+0·073	−0·014	+0·550
8	−0·079	−0·172	+0·478	+0·581
6	−0·011	−0·027	+0·002	0·000
7	+0·001	−0·004	−0·004	0·000
	Planar Anion radical		Twisted Anion radical	
1	+0·138	+0·178	−0·004	0·000
2	+0·013	−0·016	0·000	0·000
8	−0·119	−0·168	+0·004	0·000
6	+0·093	+0·067	+0·567	+0·680
7	+0·630	+0·708	−0·117	−0·360

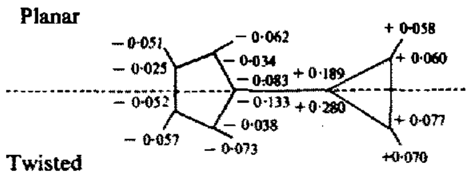

Fig 1. Total net charges calculated for neutral calicence.

Table 7 gives the carbon atom π-orbital spin densities obtained from the UHF calculations by both the INDO and the PPP calculations for the radical ions. In three out of the four cases, the agreement is very good, but for the twisted cation radical the two methods give quite different results. Though we would tend to believe the INDO results in the case of disagreement, experiment would easily distinguish between the two. It also appears that EPR experiments would have no difficulty in distinguishing between the twisted and planar form of either free radical. Another very interesting point has emerged from the INDO calculations. Although the data have not been tabulated, the calculations showed that the spin densities in the hydrogen 1s orbitals were generally in agreement with those in the π-orbitals of the attached carbon atoms, as would be required for McConnell's relation[20] to be applicable.

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