Molecular Orbital Calculations of the Stability and the Spin Density Distribution in Polymeric Aromatic Radical Ions

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Molecular orbital calculations have been performed on singly charged dimeric, trimeric, and tetrameric aromatic ions in order to estimate the stability and the unpaired spin distribution. Ordinary Hückel, extended Hückel, and the CNDO and INDO methods were used. The negative and positive species become stabilized by comparison with the isolated molecules and ions. Within the CNDO and INDO approximations the dimeric cation is more stable than the anionic species.

The sandwich geometry is the most stable of the investigated dimer geometries. In the benzene dimer cation the barrier for internal rotation around the sixfold axis is estimated to be only 0.01 eV.

In a homologous series of polymeric ions the stabilization energy decreases as the number of units increases.

The hyperfine coupling constant from the protons of the benzene dimer cation calculated by the INDO method agrees with the experimental values when a sandwich structure is assumed. For trimeric species the Hückel approach gives a spin density over the inner ring which is twice that on the outer two rings.

The existence of singly charged dimeric radical cations has recently been demonstrated by means of ESR spectroscopy.[1-6] These cations seem to be formed by an association between a monomeric ion and a neutral molecule. There is experimental evidence that the unpaired electron distribution is delocalized equally in the two partners of the system. The relative spin density distribution within each ring is similar to that of the monomer, suggesting that no major molecular distortion occurs on dimerisation. For this reason it was suggested that the two hydrocarbon rings lie in parallel planes,[2] with a geometrical arrangement similar to that of excimers. Calculations based on spectroscopic data indicate that the dimeric naphthalene ion is more stable than the individual monomer and monomer cation by 0.6 eV.[7] The kinetics of the dimerisation of the benzene ion in gas phase [8] give evidence for a stabilisation energy of at least 0.4 eV. In contrast to these results attempts to prepare dimers of negative ions have been unsuccessful.[2] This is surprising since an

intermolecular resonance integral type of interaction according to the Hückel theory predicts a stabilisation on dimerisation. The aim of the present study was to obtain predictions of the stability and of the unpaired electron distribution for a variety of geometrical models. The simple theory was used for a qualitative comparison but in order to explain differences in stability between the positive and negative complexes the inclusion of all valence electrons became necessary.

Evidence for the formation of singly charged polymeric ions is still not conclusive, but an ESR spectrum associated with a trimeric cation of coronene has been observed.[3] The calculations of trimers presented here support the finding that these are less stable than the dimer and also indicate an uneven distribution of unpaired electron density between the rings.

GENERAL REMARKS

For the purpose of molecular orbital treatment the polymeric systems are regarded as a single species. The conformation of the stable complex is probably determined by the geometry possessing the lowest total energy. Several geometries which appeared chemically probable were therefore investigated.

Hückel theory. As a first approximation the intermolecular interaction was taken into account using a resonance integral type of interaction between $2p_z$-orbitals on adjacent carbon atoms only. The intermolecular orbitals are then constructed from monomer molecular orbitals which themselves are linear combinations of the carbon $2p_z$-orbitals. The explicit form of the monomer orbitals and the corresponding energies were determined from ordinary Hückel theory. The stabilisation energy of a dimeric radical ion A_2^+ can be defined as [6]

$$\Delta E^+ = E(A_2^+) - E(A) - E(A^+) \tag{1}$$

The same general procedure has already been applied to the treatment of excimer luminescence energy.[9] In this simple treatment a reliable estimate cannot be made of the equilibrium distance between two interacting atoms in different rings. However, the assumptions underlying the Hückel method are scarcely in accordance with a very short or very long separation. Thus the distance was assumed to have a value similar to that between opposing atoms of the interacting benzene rings in the paracyclophane anion,[10] that is about 3 Å. By comparison an empirical estimate of the intermolecular resonance integral from the optical spectrum of the naphthalene dimer cation [7] yields $\beta' \sim 5000$ cm^{-1}.[6] This gives an estimated interplanar distance of 3.2 Å.[9]

To obtain Hückel energies and orbitals the ratio $\beta'/\beta = 0.2$ was adopted from the estimate of $\beta = -3$ eV for the intramolecular resonance integral.

CNDO and INDO methods. As a second approximation all valence electrons were taken into account using the self consistent field molecular orbital methods devised by Pople *et al.*[11],[12] In these methods differential overlap is neglected. Two-electron integrals are evaluated using Slater atomic orbitals, while the one-electron integrals are selected empirically. A computer programme written by Dobosh [13] affords versions for open and closed shell calculations at both

the CNDO and INDO levels of approximation. These methods are simple enough to permit calculations for dimeric benzene ions.

Using the CNDO method [11] several geometries were considered in which the distances between the interacting rings were assumed to be different. The intramolecular bond lengths used were those of the benzene molecule. The total energy of a given geometry was compared to that of the separated ion and neutral molecule; the stabilisation energy is as defined in eqn. (1). Programme and computer limitations prevent use of the method for calculations on larger complexes such as the dimeric naphthalene and coronene ions.

The INDO method [12] was used to estimate spin densities and hyperfine coupling constants. In this treatment the one-center exchange integrals are retained, which leads to a non-vanishing spin density in the σ orbitals. The coupling constants calculated from the spin densities have been found to agree quite well with experimental values.[12] In this study calculations on dimeric benzene ions were made for different geometries, but with a fixed interplanar distance of 3 Å between the interacting rings. In the complexes possessing D_{6h} or S_{12} symmetry, treated below, the electronic ground state is degenerate, implying the appearance of a Jahn-Teller distortion. The noticeable effect on the coupling constants is generally small. The calculated values are averages made over slightly distorted Jahn-Teller components.

Extended Hückel method. Previous investigations have shown that the retention of an intermolecular overlap is necessary to account properly for the interaction between molecules. The stability of excimers has been qualitatively accounted for by extended Hückel calculations. The aim with the calculations presented here was to investigate whether a qualitative description of the dimeric benzene ions could be obtained from the simple one-electron model modified to include overlap. This was made possible using a computer programme [14] which performs calculations according to the extended Hückel method. The parameters used were selected according to the original treatment of Hoffmann.[15] In view of the results obtained with the benzene dimers, an extension to larger systems was considered unjustified.

RESULTS

Dimeric benzene ions

Six different geometries were investigated (Fig. 1). In four of them the rings lie in two parallel planes. The sandwich complex (I) has the same symmetry D_{6h} as the monomer. The geometry (II) is obtained by rotating one of the rings through 30° about its sixfold axis. A displacement of one of the rings along the x or y axes yields a complex with C_{2h} symmetry. One possible arrangement arises when C_1 and C_6 of the upper ring are situated above C_1' and C_6' of the lower ring, model III. In model IV, C_1 and C_1' oppose each other. In models V and VI the rings are coplanar with a naphthalene- or biphenyllike arrangement with point group symmetry D_{2h}.

Stabilities. Since the Hückel calculations are only qualitative the stabilisation energies of Table 1 correspond to the approximation when terms of the order β'/β are neglected. In model II one in each pair of rings is rotated through
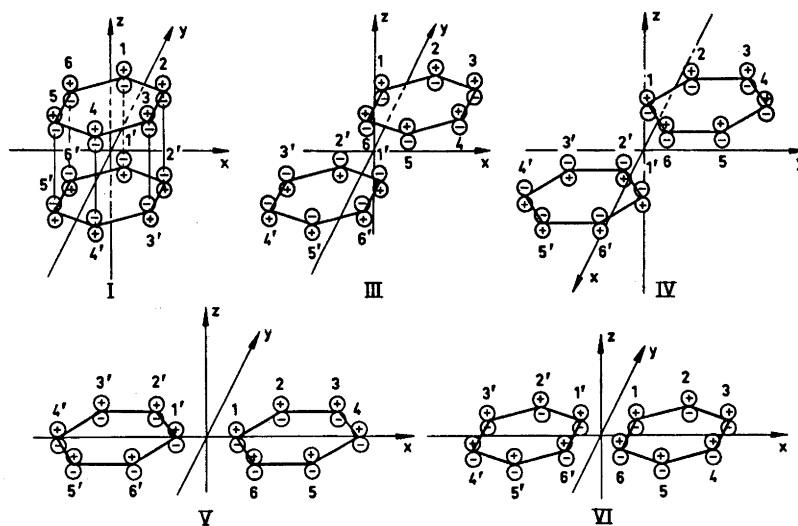
Fig. 1. Structure of dimeric benzene models. Model II (not shown) is obtained by rotating one of the rings in I through 30° about the *z*-axis.

Table 1. Stabilization energies of dimeric, trimeric and tetrameric ions calculated from methods described in the text.

Compound	HMO (β')	ΔE^+ INDO [a] (eV)	EHT [b] (eV)	HMO (β')	ΔE^- INDO [a] (eV)	EHT [b] (eV)
Dimers						
Benzene I	1	−1.94	−0.049	1	−0.29	−0.027
II	$\sqrt{3}$ [c]	−1.93	−0.047	1 [c]		−0.014
III	1/2	[d]	−0.028	1/2		+0.037
IV	1/3	−1.26	−0.054	1/3		−0.017
V			+1.13			+1.98
VI			+0.74			+1.71
Naphthalene I	1			1		
II	$(5+\sqrt{5})/20$			$(5+\sqrt{5})/20$		
Coronene I	1			1		
Polymers						
Benzene trimer	$\sqrt{2}$			$\sqrt{2}$		
Benzene tetramer	$(1+\sqrt{5})/2$			$(1+\sqrt{5})/2$		

[a] With interplanar distance $d=3.0$ Å. [b] $d=3.6$ Å for models I—IV; the shortest intermolecular C···C' distance in V and VI is 3.2 Å. [c] The value of β' may differ from that of the other models since the $2p_z$-orbitals do not directly overlap. [d] No data owing to convergence difficulties.

30° with respect to the other. Accordingly each atom has two atoms from the adjacent ring as nearest neighbours. In all other Hückel calculations only interaction between opposing atoms was assumed. The value of β' is also different in model II since the type of intermolecular bonding differs from that in the other models. Steric repulsion between hydrogen atoms prevents application of the simple theory to models V and VI.

The CNDO calculations with model I predict equilibrium interplanar distances of $d = 2.2$ Å for the positive ion and $d = 2.5$ Å for the negative complex. The corresponding stabilisation energies are $\Delta E^+ = -4.63$ eV, $\Delta E^- = -1.12$ eV. For a shorter distance of $d = 1.6$ Å, very large stabilities are predicted both for the positive and the negative ion as well as for the uncharged complex. The results of these calculations are not reproduced in Table 1 which lists only the stabilisation energies with a fixed value of $d = 3.0$ Å employing the INDO method. The stabilisation energy obtained by applying the extended Hückel theory was evaluated for models I−IV using the equilibrium distance of $d = 3.6$ Å obtained for model I in specific calculations. The energy of V and VI was evaluated for a minimum intermolecular $C \cdots C'$ distance of 3.2 Å.

Spin densities and coupling constants. In the Hückel treatment the coupling constants are evaluated from McConnells relationship $a = Q \times \varrho^\pi$. In the monomeric cation $|a| = 4.44$ G, which with $\varrho^\pi = 1/6$ yields $|Q| = 26.7$ G.

The coupling constants obtained from the INDO calculations are estimated from the spin density in the hydrogen $1s$-orbitals. The coupling constants of model III are not reported here because of convergence difficulties with the calculations. For the negative complex only model I was considered.

Dimeric naphthalene ions

Two different models were investigated. Model I has the two molecules in parallel planes so that the monomer units cover each other completely as shown in Fig. 2a. This structure belongs to the same point group D_{2h} as the naphthalene molecule. The second model also has the two molecules in parallel planes, but they are displaced so that only one of the rings of the first monomer unit covers a ring of the second unit, Fig. 2b. The symmetry is C_{2h}.
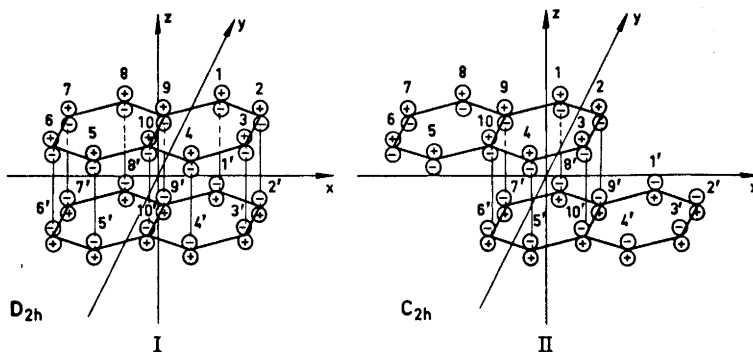

Fig. 2. Structure of dimeric naphthalene models.

Stability. The Hückel theory was the only method attempted. For model II the stabilisation energy depends on the ratio β'/β. The value in Table 1 corresponds to the assumption that $\beta'/\beta \ll 1$.

Table 2. Hyperfine coupling constants for dimeric and trimeric ions.

Compound	Model	Positions	H coupling constant (G) HMO [a]	INDO
(Benzene)$_2^+$	I	All	-2.2	-1.9
	II	All	-2.2	-1.9
	III	(1, 6, 1', 6')	-3.0	$-$
		(2, 5, 2', 5')	0.0	$-$
		(3, 4, 3', 4')	-3.6	$-$
	IV	(1, 1')	-4.3	-4.8
		(2, 6, 2', 6')	-1.4	-1.4
		(3, 5, 3', 5')	-1.0	$+0.3$
		(4, 4')	-4.4	-4.4
(Benzene)$^-$		All		-3.6^b
(Benzene)$_2^-$		All		-1.8
(Naphthalene)$_2^+$	I	(1, 4, 5, 8, 1', 4', 5', 8')	-2.8	
		(2, 3, 6, 7, 2', 3', 6', 7')	-1.1	
	II	(1, 4, 5', 8')	-3.5	
		(2, 3, 6', 7')	-1.4	
		(5, 8, 1', 4')	-1.9	
		(6, 7, 2', 3')	-0.8	
		(9, 10, 9', 10')	0.0	
(Benzene)$_2^+$		Central molecule	-2.2	
		Outer molecules	-1.1	
(Benzene)$_4^+$		Central molecules	-0.6	
		Outer molecules	-1.6	
(Ethylene)$_2^+$		All		-4.6
(Ethylene)$_3^+$		Central molecule		-5.9
		Outer molecules		-1.9

[a] Coupling constants were estimated from π electron spin densities calculated using $\beta'=0.2$ β with $a=Q \cdot \varrho$. For benzene ions $Q=-26.7$ G, for naphthalene ions $Q=-30.3$ G. [b] Ref. 12.
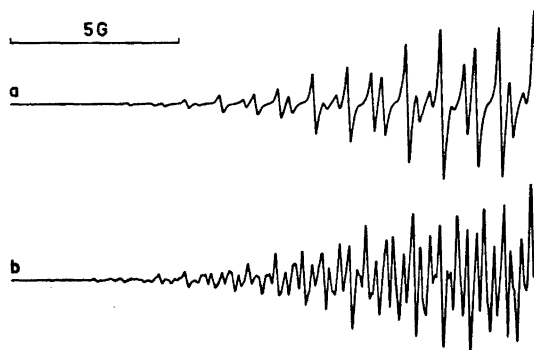

Fig. 3. Computed line shapes for dimeric naphthalene cation. (a) For model I using $a_1=2.77$ G (8H), $a_2=1.03$ G (8H). (b) For model II using $a_1=3.50$ G (4H), $a_2=1.89$ G (4H), $a_3=1.40$ G (4H), $a_4=0.78$ G (4H); $(\beta'/\beta=0.2)$.

Spin densities and coupling constants. In model I the spin densities become exactly one half of those in the monomer ion. With the lower symmetry of model II the spin densities depend on the ratio β'/β. The value $\beta'/\beta = 0.2$ was used together with a suitable estimate of $Q = -30.3$ G to obtain the coupling constants of Table 2. By this choice of Q the experimental splittings [1] of the dimeric complex is closely reproduced by the calculated values for model I. Simulated spectra using experimental values for the couplings and line width are compared in Fig. 3 with that predicted for model II.

Dimeric coronene ion

Due to the complexity of the monomer units the only model to be considered is the sandwich arrangement which possesses the same symmetry D_{6h} as the monomer units. Only the Hückel theory can feasibly be applied. The stabilisation energy $\Delta E^\pm = \beta'$ is equal for the positive and the negative ions. The spin densities become one half of those in the monomeric ion.

Trimeric and tetrameric ions

The only model of trimeric benzene investigated has the sandwich type structure with D_{6h} symmetry. The benzene rings are placed parallel with each other as indicated in Fig. 4. This is the same arrangement as that used for the model I dimer. The calculations performed with the Hückel theory yield a stabilisation energy of $\Delta E^\pm = \sqrt{2}\beta'$. The spin density becomes twice as high in the central unit as in the outer rings.

Completely analogous results were obtained for the coronene trimer.

A sandwich type of structure in which four benzene rings are parallel as in the model I dimer and the trimer with D_{6h} symmetry (Fig. 4) was also in-
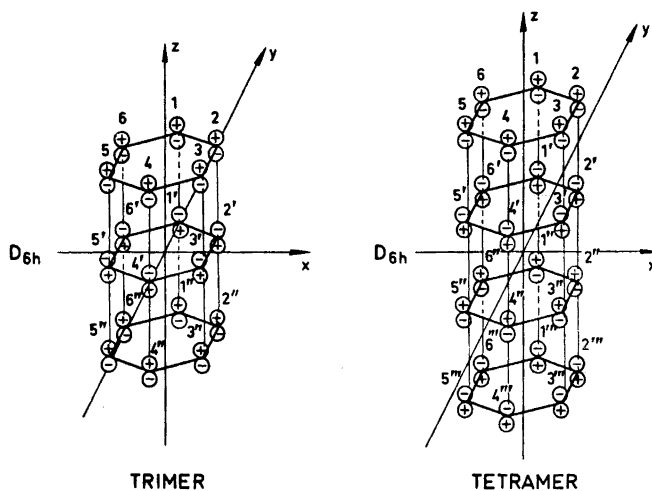

Fig. 4. Structure of trimeric and tetrameric benzene models.

vestigated with regard to its stability (Table 1). In this case also an uneven spin density distribution between the inner and outer rings is predicted (Table 2), the ratio being $\varrho_{inner}/\varrho_{outer} = 0.38$.

INDO calculations carried out for the trimeric cation of ethylene with an intermolecular distance of 2.5 Å predicts a stabilisation energy of $\Delta E^+ = -1.44$ eV against the decomposition

$$(C_2H_4)_3^+ \rightarrow (C_2H_4)_2^+ + C_2H_4$$
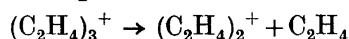
For the dimeric cation $\Delta E^+ = -5.94$ eV. These calculations yield an uneven spin distribution between the monomer units (Table 2).

DISCUSSION

Stability. From the preceding calculations it is clear that the dimeric and polymeric ions become stabilised by comparison with the individual monomer units. Due to the very rough approximations, necessitated by the complex nature of the compounds investigated, the main emphasis will be placed on the qualitative results obtained. The merits of each method will be discussed only briefly.

With only one exception the data of Table 1 demonstrate a decreased stability when the symmetry of the dimeric complex is lowered. This tendency is not unexpected since the intermolecular overlap becomes less effective. The naphthalene or biphenyl like arrangements are not stable in the EHT scheme probably as a consequence of the repulsion between neighbouring hydrogens on each molecule. It appears that the sandwich geometry is the most stable. However, the structure is probably not completely rigid. Thus the INDO calculation yields a barrier of only 0.01 eV for internal rotation around the sixfold axis in the benzene dimeric cation. This indicates that rapid reorientation occurs even at rather low temperatures.

The stability of polymeric ions with the same general structure decreases as the number of monomeric units constituting the species increases. Thus, according to the Hückel theory the energy required to remove a neutral monomer molecule is β', 0.41 β', and 0.20 β' for the dimeric, trimeric, and tetrameric benzene ions which possess a D_{6h} structure. This result is supported by the INDO calculations on ethylene dimeric and trimeric positive ions. Experimentally, a line broadening of the ESR spectrum assigned to the trimeric coronene cation occurs with increasing temperature which indicates a rather short lifetime for the complex.[3] The lifetime of the ion clusters $(C_2H_4)_n^+$ detected in the mass spectrometer [16] also becomes less as the number of monomer units increases.

In most cases the Hückel theory predicts the same stability for the anions as for the cations. This does not conform with experimental findings; so far no observations of negative dimers have been reported. The assumption made in the Hückel theory, that total energies may be approximated by adding orbital energies, is reasonable only for neutral molecules.[17] For ionic species an SCF treatment is required. In fact the INDO method predicts a considerably higher stability for the positive dimeric benzene ion than for the negative complex.

The large stabilities predicted at short intermolecular distances by the CNDO method are obviously in error. These inaccuracies may contribute to a diminishing extent as the separation increases. However, excessively high values are obtained both for the stability at the equilibrium distance and that calculated by the INDO method when the molecules are farther apart. The equilibrium distance is evidently underestimated as compared with the value estimated for excimer complexes.

The importance of retaining intermolecular overlap in order to make satisfactory estimates of intermolecular interaction energies has previously been demonstrated.[18] A perturbation treatment using the Hückel theory yields a repulsion which is a second order interaction in the overlap for interacting molecules in their ground state. When one molecule is excited an additional first order stabilising effect is predicted.[18] This also applies to systems containing an unpaired electron. The extended Hückel method should yield comparable results [18] and thus a minimum in the interaction energy at a specific interplanar distance. However, the estimated stability appears to be too low by an order of magnitude. Although the interaction energy ΔE_0 of the neutral complex A_2 is probably reasonably accounted for by the extended Hückel method the ionization potential I is not.[15] Accordingly the stability given by $\Delta E^+ = \Delta E_0 + I(A) - I(A_2)$ may be subject to large errors.

Spin densities and coupling constants. The coupling constants obtained by the Hückel theory agree rather well with those calculated by the INDO method. The qualitative predictions of this simple method may thus be useful for treating large complexes where the more refined method is inapplicable.

There is no significant difference between the coupling constants estimated by the INDO method for models I and II of the benzene dimeric cation. This shows that internal rotation may take place without affecting the ESR spectrum. The agreement with the experimental value [4a] $|a| = 2.1$ G is also within the acceptable error of 10 %. The distorted models III and IV yield couplings which are at variance with experimental data. For the naphthalene dimeric ion the distortion to C_{2h} symmetry has a less pronounced effect on the spin density distribution. Nevertheless, comparison of theoretical spectra for the two geometries I and II with the experimental line profile indicates that the sandwich model is the more likely.

The marked change in spin population for benzene dimeric ions is associated with the effect of substituents in benzene anions.[19] According to the Hückel theory the degeneracy of the antibonding e_{2u} level in this instance is removed and the unpaired electron is confined to the orbital possessing the lowest energy. The remarkable sensitivity of the spin distribution to exceedingly small perturbations has previously been demonstrated.[19] In models III and IV the unpaired electron of the cation occupies the minus combination of the monomer orbitals having the approximative form

$$\phi_1(e_{1g}) = \tfrac{1}{2}\{p_{z1} - p_{z3} - p_{z4} + p_{z6}\} \hspace{2cm} \text{(model IV)}$$
$$\phi_2(e_{1g}) = (1/\sqrt{12})\{2p_{z1} + p_{z2} - p_{z3} - 2p_{z4} - p_{z5} + p_{z6}\} \hspace{1cm} \text{(model III)}$$

Experimental data do not give any evidence for such distortions.

Trimeric cations belonging to the point group D_{6h} symmetry require that the orbital containing the unpaired electron is of the type

$$\psi = a\phi_{\Gamma'} - b(\phi_{\Gamma} + \phi_{\Gamma''})$$ (2)

Here ϕ_{Γ} represents the π-orbital carrying the odd electron in the monomeric ion. The Hückel theory yields $a = 1/\sqrt{2}$, $b = 1/2$. Thus the spectrum of the trimeric coronene cation [3] is expected to possess one set of lines, due to the 12 protons in the central ring, separated by half the splitting of the monomeric ion $a_1 = 1.57/2 = 0.78$ G, each line being further split by $a_2 = 1.57/4 = 0.39$ G into 25 components. The experimental data available [3] suggest that this estimate is in error. An assignment of the experimental line profile with $a_1 = 1.2$ G, $a_2 = 0.15$ G is not unreasonable. The overall splitting $\Delta H_0 = 12 \times 1.2 + 24 \times 0.15 = 18.0$ G then becomes comparable with $\Delta H_0 = 12 \times 1.57 = 18.8$ G for the monomer cation. The constancy of these values would hold strictly if the unpaired electron were entirely localized to an orbital of the type (2) and if the splitting constants could be obtained using a fixed value of Q in McConnell's relation.

The coupling constants calculated for the dimeric and trimeric ethylene cations demonstrate that this rule also holds approximately when the more refined INDO method is used. Moreover the ratio $a_1/a_2 = 3.0$; this is greater than the value 2.0 obtained by applying the Hückel theory. SCF calculations on systems containing larger molecules is impractical at present.

Since no ESR spectrum of tetrameric benzene ions has been observed the validity of the spectral predictions of Table 2 will not be considered at present.

CONCLUSIONS

The main findings may be summarized as follows.

(a) Among the geometries of dimeric ions investigated the sandwich type possesses the highest stability. In the benzene dimeric cation the structure is not completely rigid since the barrier for internal rotation around the hexad axis is only 0.01 eV.

(b) The stability of positive dimers is greater than that of the negative complex.

(c) Equilibrium distances and energies cannot be successfully calculated by any of the methods used here. A modified SCF treatment which takes into account intermolecular orbital overlap may be more satisfactory.

(d) When an "empirical" intermolecular distance of 3 Å is selected the experimental proton hyperfine couplings of the dimer may be reasonably reproduced in INDO calculations. The correct prediction of spin distribution in trimeric ions does not seem possible on the basis of the simple Hückel theory.

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