

more or less, wrapped around the plane of N(3) and N(4), producing the shorter van der Waals contacts. In contrast to this, the terminal atoms N(1) and N(2) always lie on the convex side of neighboring molecules and are not involved in any intermolecular distances less than 3.4 Å.

That these short contacts to only one side of the molecule have little or no effect on the over-all molecular structure is evidenced by the C_{2v} molecular sym-

metry and by the existence of a single $C\equiv N$ band in the infrared spectrum.¹

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Electronic Spectrum of Cyclononatetraenide

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The electronic spectrum of cyclononatetraenide ($C_9H_9^-$), a monocycle possessing a ninefold rotation axis, has been measured. The tetraethylammonium salt shows only two regions of absorption from -33 to 25° in acetonitrile: an intense, structureless absorption at $250 m\mu$ (ϵ 66,300) and a weaker, resolved system centered at $320 m\mu$ (ϵ 6700). Theoretical analysis of the spectrum expected for planar $C_9H_9^-$ (D_{9h}) shows good agreement with that obtained experimentally. The high-energy band is the only allowed transition (${}^1E_1'$) in the spectrum, but it can be shown that vibronic coupling imparts a transition moment of the observed magnitude to the low-energy band.

Introduction

Cyclononatetraenide¹ is an odd nonalternant monocycle of nine carbons and ten π -electrons. N.m.r. evidence favors a planar, nonagonal structure, although this implies 180° of classical angle strain in the σ -framework. The purpose of this paper is the consideration of the electronic spectrum of this molecule, which is shown to be in accord with theoretical expectation for the planar structure.

Since cyclononatetraenide bears a negative charge and is subject to destructive hydrolysis by amphiprotic solvents, its spectrum could be obtained only in aprotic organic solvents. Spectra of alkali metal and tetraethylammonium salts in tetrahydrofuran and acetonitrile solutions, respectively, revealed two regions of absorption: an intense, structureless band at $250 m\mu$ (ϵ 66,300) and a much weaker absorption at $320 m\mu$. The weak band was resolved for the tetraethylammonium salt in acetonitrile with major components at $317 m\mu$ (ϵ 6630) and $322 m\mu$ (ϵ 6750) (Figure 1).

Theory and Calculations

The theory of the electronic states of the even alternant monocycles containing $(4n + 2)$ π -electrons is well understood from the work of Platt² and Moffitt.³

(1) E. A. LaLancette and R. E. Benson, *J. Am. Chem. Soc.*, **85**, 2853 (1963); T. J. Katz and P. J. Garratt, *ibid.*, **85**, 2852 (1963).
(2) J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949).

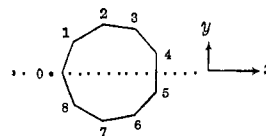
Odd nonalternant monocyclic systems have been studied less thoroughly, although from the original work of Hückel⁴ it was possible to predict that the $(4n + 2)$ ions, $C_3H_3^+$, $C_5H_5^-$, $C_7H_7^+$, $C_8H_8^{-2}$, and $C_9H_9^-$, would have closed-shell ground states and be potentially capable of synthesis. The C_3 - C_8 ions have been considered previously by Longuet-Higgins and McEwen.⁵

Planar $C_9H_9^-$ belongs to the D_{9h} -symmetry point group (character table given in Table I) and possesses the highest rotation axis yet encountered in a small molecule. The self-consistent molecular orbitals are determined fully by the C_9 subgroup and can be written in the form⁶

$$\psi_\xi = \sigma_\xi \sum_{m=0}^8 \omega^{m\xi} \phi_m \quad (\xi = 0, \pm 1, \pm 2, \pm 3, \pm 4) \quad (1)$$

$$\omega = \exp(2\pi i/9)$$

where the ϕ_m 's are carbon $2p\pi$ -AO's numbered as shown, and the σ_ξ are normalizing constants equal to



$1/\sqrt{9}$ for all ξ when overlap is neglected. Under D_{9h} the molecular orbitals transform as

$$\psi_0 \longrightarrow a_2''$$

$$\psi_{\pm|\xi|} \longrightarrow e_{|\xi|}'' \quad (\xi = 1, 2, 3, 4)$$

The closed-shell ground state (${}^1A_1'$) is given by the configuration

$$\text{ground state: } \psi_0^2 \psi_{+1}^2 \psi_{-1}^2 \psi_{+2}^2 \psi_{-2}^2$$

which with the neglect of overlap corresponds to the configurational wave function

(3) W. Moffitt, *ibid.*, **22**, 320 (1954).
(4) E. Hückel, *Z. Physik*, **70**, 204 (1931).
(5) H. C. Longuet-Higgins and K. L. McEwen, *J. Chem. Phys.*, **26**, 719 (1957).
(6) The subsequent notation conforms closely to that of Moffitt³ for comparison purposes.

Table I. D_{9h} Point Group Character Table^a

	E	$2C_9$	$2C_9^2$	$2C_9^3$	$2C_9^4$	$9C_2$	σ_h	$9\sigma_v$	$2S_9$	$2S_9^2$	$2S_9^3$	$2S_9^4$
A_1'	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1
A_1''	+1	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	-1
A_2'	+1	+1	+1	+1	+1	-1	+1	-1	+1	+1	+1	+1 R_z
A_2''	+1	+1	+1	+1	+1	-1	-1	+1	-1	-1	-1	-1 z
E_1'	+2	$2Z_1$	$2Z_2$	$2Z_3$	$2Z_4$	0	+2	0	$2Z_1$	$2Z_2$	$2Z_3$	$2Z_4$ (x, y)
E_1''	+2	$2Z_1$	$2Z_2$	$2Z_3$	$2Z_4$	0	-2	0	$-2Z_1$	$-2Z_2$	$-2Z_3$	$-2Z_4$ (R_x, R_y)
E_2'	+2	$2Z_2$	$2Z_4$	$2Z_6$	$2Z_8$	0	+2	0	$2Z_2$	$2Z_4$	$2Z_6$	$2Z_8$
E_2''	+2	$2Z_2$	$2Z_4$	$2Z_6$	$2Z_8$	0	-2	0	$-2Z_2$	$-2Z_4$	$-2Z_6$	$-2Z_8$
E_3'	+2	$2Z_3$	$2Z_6$	$2Z_9$	$2Z_{12}$	0	+2	0	$2Z_3$	$2Z_6$	$2Z_9$	$2Z_{12}$
E_3''	+2	$2Z_3$	$2Z_6$	$2Z_9$	$2Z_{12}$	0	-2	0	$-2Z_3$	$-2Z_6$	$-2Z_9$	$-2Z_{12}$
E_4'	+2	$2Z_4$	$2Z_8$	$2Z_{12}$	$2Z_{16}$	0	+2	0	$2Z_4$	$2Z_8$	$2Z_{12}$	$2Z_{16}$
E_4''	+2	$2Z_4$	$2Z_8$	$2Z_{12}$	$2Z_{16}$	0	-2	0	$-2Z_4$	$-2Z_8$	$-2Z_{12}$	$-2Z_{16}$

^a The table is given in real form for computational purposes, but the discussion developed through eq. 1 employs the complex orbitals; $Z_n = \cos 2n\pi/9$.

$$V_0 = (9!)^{-1/2} \det[\psi_0(1)\bar{\psi}_0(2) \dots \psi_{-2}(9)\bar{\psi}_{-2}(10)]$$

$$= |0\bar{0}1+\bar{1}+1-\bar{1}-2+\bar{2}+2-\bar{2}-|$$

where the symbols have the usual meanings. Each singly excited configuration gives rise to a singlet (S) and triplet (T) wave function of the form

$$S_{ik}' = 2^{-1/2} [|0\bar{0} \dots i\bar{k}' \dots | \mp |0\bar{0} \dots \bar{i}k' \dots |]$$

$$T_{ik}'$$

where the upper sign refers to the singlet and k' is an orbital unoccupied in the ground state (3^\pm or 4^\pm). These 21 singlet and 20 triplet wave functions form the basis for the configuration interaction (CI) description of $C_9H_9^-$. First-order CI which involves the promotion $2^\pm \rightarrow 3^\pm$ gives rise to the states ${}^1,3E_1'$ and ${}^1,3E_4'$. Of the remaining 17 singlet configurations, none has E_1' symmetry which is necessary for an allowed purely electronic transition.

When the Hamiltonian is unspecified, the Hückel orbital energies ϵ_ξ and symmetries are immediately determined and are given in Table II along with those of

Table II. Orbital Energies ϵ_ξ and Symmetries

C_6H_6			$C_9H_9^-$			
ξ	ϵ_ξ^a	Symmetry	ξ	ϵ_ξ^a	$\epsilon_{SCF, e.v.}$	Symmetry
0	-2.000	a_{1u}	0	-2.000	-9.994	a_2''
± 1	-1.000	e_{1g}	± 1	-1.532	-8.716	e_1''
± 2	+1.000	e_{2u}	± 2	-0.347	-4.881	e_2''
3	+2.000	b_{1g}	± 3	+1.000	+3.510	e_3''
			± 4	+1.879	+6.652	e_4''

^a In units β^{-1} .

benzene for comparison. As is well known, when spin-free AO's are used in building ψ_ξ , no distinction of state multiplicity arises; further, the neglect of the electron repulsion operator results in complete degeneracy of the four lowest excited configurations (see Figure 2). These effects are taken into account by the antisymmetrized molecular orbital wave functions S_{ik}' , and the necessary energies were calculated using the full π -electron Hamiltonian according to the method of Pariser and Parr.^{7,8} It was assumed that the carbon-carbon bond length is 1.397 Å, the benzene value.

(7) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466 (1953), and later papers.

(8) R. Pariser, *ibid.*, **24**, 250 (1956).

Figure 2 shows that inclusion of electron repulsion effects does not remove the degeneracy of the resulting

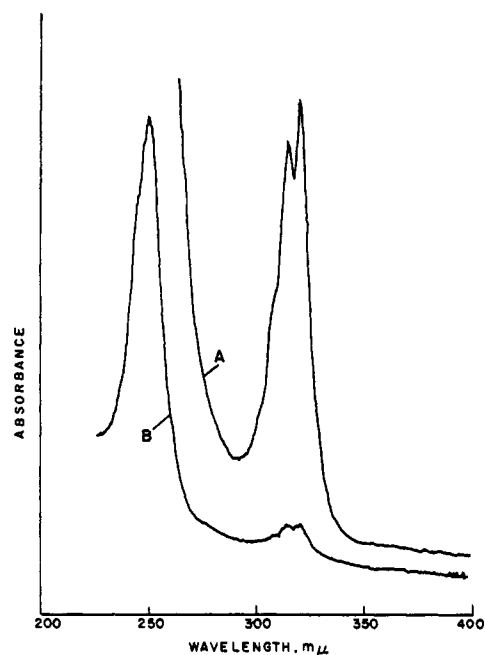


Figure 1. Ultraviolet spectrum of tetramethylammonium cyclononatetraenide in acetonitrile solution at -33° (Cary 14 spectrophotometer; concentration for curve A is ten times that of B).

functions $S_{+2,+3}$, $S_{-2,-3}$, and $S_{-2,+3}$. This result can be shown to hold generally for the odd-alternant monocycles and is a consequence of symmetry. When first-order CI is taken into account, these four levels are split into the doubly degenerate states E_4' (3.619 e.v.) and E_1' (5.446 e.v.).⁹ A purely electronic transition is allowed only to ${}^1E_1'$ (Table III) and is polarized in the molecular plane. This prediction is in reasonable agreement with experiment which finds two levels at 4.96 and 3.88 e.v. (band center). Transition to the former is very intense and must be assigned ${}^1E_1'$. The long wave-length absorption is only one-tenth the intensity of the high energy band and can be assigned to the electronically symmetry forbidden ${}^1E_4'$ transition. In benzene, first-order CI is more effective in removing

(9) Values of the quantum mechanical integrals used in the calculations in this paper and details of the method are given by H. E. Simmons, *ibid.*, **40**, 3554 (1964).

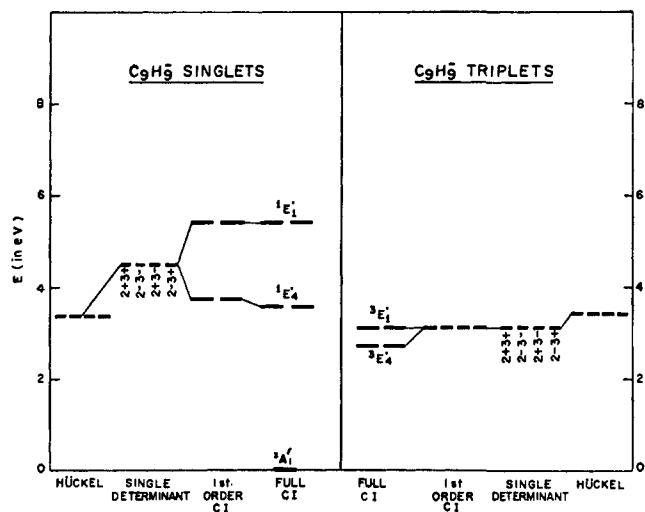


Figure 2. Energy levels of $C_9H_9^-$. The location of the Hückel states is only approximate. Full CI signifies configuration interaction between all *singly* excited configurations.

the degeneracy and results in two low-lying states, ${}^1B_{2u}$ and ${}^1B_{1u}$, transitions to both of which are electronically symmetry forbidden (Figure 3).

Table III. Lower Electronic States of $C_9H_9^-$

State ^a	$r = 1.397 \text{ \AA.}$	
	E , e.v.	f^b
${}^1A_1'$	0	Ref.
${}^1E_4'$	3.619	0.000
${}^1E_1'$	5.446	1.987
${}^1E_3'$	6.601	0.000
${}^1E_2'$	6.697	0.000
${}^1E_4'$	7.532	0.000
${}^1E_2'$	7.847	0.000
${}^3E_4'$	2.756	Ref.
${}^3E_1'$	3.039	0.000
${}^3E_2'$	5.275	0.000

^a Only the lowest few states are given. ^b Theoretical oscillator strength.

The lowest triplet state is predicted to have E_4' symmetry and to lie 2.756 e.v. above the ground state. No absorption is found or expected in this region ($\sim 450 \text{ m}\mu$).

Since the determinantal wave functions were built from one-electron molecular orbitals which are the SCF orbitals in this case, no configurational mixing with the ground state occurs. The full CI calculation of the singlet and triplet states arising from all singly excited configurations was carried out and the results are shown in Table III.⁹ An SCF calculation according to the method of Pople¹⁰ was also carried out using the same molecular integrals,⁹ and the SCF energies are given in Table II. Since the SCF bond order is $\rho_{SCF} = 0.6399$, indicating a bond length of 1.403 \AA. by the empirical relation of Coulson,¹¹ the CI calculation was repeated with this carbon-carbon distance. The results were virtually unchanged, as expected, except for the higher states. The lower states were found at 3.576 (${}^1E_4'$), 5.413 (${}^1E_1'$), and 2.712 e.v. (${}^3E_4'$).

(10) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).

(11) C. A. Coulson, "Valence," Oxford at the Clarendon Press, London, 1953, Chapter IX.

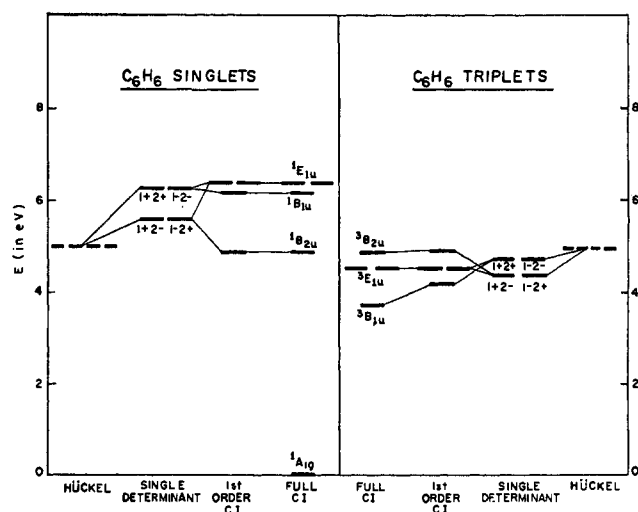


Figure 3. Energy levels of C_6H_6 . The location of the Hückel states is only approximate. Full CI signifies configuration interaction between all *singly* excited configurations.

The theoretical oscillator strength of the ${}^1E_1' \leftarrow {}^1A_1'$ transition is 1.99 which is in accord with the high intensity found for this transition ($\epsilon 66,300$). The ratio of the theoretical oscillator strength of the ${}^1E_1'$ absorption to the value for the corresponding ${}^1E_{1u}$ transition in benzene computed in the same manner is ($f_{e1'}/f_{e1u}$) ~ 1.8 . This value is in fair agreement with the ratio of the experimental extinction coefficients ($\epsilon_{e1'}/\epsilon_{e1u}$) ~ 1.4 . Better agreement was not expected since $C_9H_9^-$ is charged, and ionic interaction with the solvent will strongly influence properties such as molar extinction coefficients.

Vibronic Interactions

Under "odd" perturbations, such as distortions of the nine-membered ring caused by vibrations, mixing of E_1' and E_4' can occur with suitable vibrations so that the transition ${}^1E_4' \leftarrow {}^1A_1'$ becomes vibronically allowed. The perturbation theory developed by Moffitt³ shows that the twofold degenerate ${}^1E_4'$ and ${}^1E_1'$ states are split equally by the application of a molecular distortion of specified amplitude and symmetry. In the present case, for example, vibrations of symmetry E_4' and E_3' may couple the degenerate electronic states. Such vibrations occur in which bond lengths vary around the cyclic system; in Moffitt's language this would be represented by a sum of one-electron perturbing operators affecting the one-electron resonance integrals. Since two vibrational modes may cause coupling, the energies found from solving the preceding secular determinant will be a function of the two amplitudes of vibration. The results for various pairs of amplitudes can be expressed by exhibiting the corresponding potential energy *surfaces*. The dynamic vibrational motions of the molecule are determined from the topological features of these surfaces.

There are two questions which must be answered in order to further describe a molecular system in which vibronic coupling has removed electronic degeneracy. To begin with, it is assumed that in the absence of the coupling perturbation there exists one minimum on each of the energy surfaces corresponding to the undistorted molecule. The first question is whether or not new

minima are produced upon introduction of the coupling perturbation. Secondly, are the new minima "deep" enough to allow the molecule to take up new, distorted equilibrium positions about which to vibrate or are the minima shallow so that a complicated pattern of vibrational motion emerges, *i.e.*, a dynamic Jahn-Teller effect?¹² In the case where two degenerate states are directly coupled by a given vibration, a perturbation linear in the vibrational amplitude will always produce new minima in the potential energy surface and one must then proceed to the question of whether the static or dynamic Jahn-Teller effect obtains. In the situation under consideration, however, such is not the case. Here there is no one-electron term which can couple degenerate states directly; the degeneracies of the ${}^1E_1'$ and ${}^1E_4'$ levels are removed by coupling between states in different manifolds as indicated in the preceding secular determinant. The difference arises from the fact that the initial energy separation of the unperturbed levels weakens the effect of their resultant coupling upon introduction of the perturbation. The farther apart the two manifolds, the less likely it is that new minima will be produced. Furthermore, when just the two pairs of degenerate states are involved the effect of the perturbation can only move the upper states to higher energy, so it is clear that it is not possible in any event for these states to exhibit new minima.

The purpose of the preceding discussion is to point out the complications involved in adequately treating even relatively simple systems. In the present example it was found using the approach of Hobey and MacLachlan¹³ that no new minima are predicted for the cyclononatetraene anion excited states under consideration. Of course, even in the absence of new minima, vibrations of the molecule about its equilibrium position will lead to vibrationally allowed transitions.¹⁴ If reasonable average amplitudes of zero-point oscillation are assumed, a ratio of extinction coefficients for the strongly allowed (${}^1E_1' \leftarrow {}^1A_1'$) to weakly allowed (${}^1E_4' \leftarrow {}^1A_1'$) transitions of about 9 was obtained. This confirms the origin and general nature of the observed spectra.

The Ground State

Perhaps the most remarkable aspect of cyclononatetraenide is its existence. The framework σ -orbitals are formally subject to 180° of classical angle strain based on trigonal hybrids, and thus far physical measurements have given no evidence to question a planar, nonagonal structure. Low temperature n.m.r. studies have revealed no line broadening of the single sharp proton resonance at 6.72 p.p.m.¹⁵; however, these experiments do not yet preclude rapid oscillation between structures of lower symmetry. The simple electronic spectrum discussed above provides support for the proposed D_{9h} symmetry; however, a slightly puckered structure of D_{3h} symmetry would be expected to have a similar electronic spectrum.

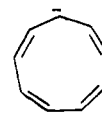
(12) See, for example, (a) H. C. Longuet-Higgins, U. Öpik, M. H. L. Pryce, and R. A. Sack, *Proc. Roy. Soc. (London)*, **A244**, 1 (1958); (b) W. Moffitt and A. D. Liehr, *Phys. Rev.*, **106**, 1195 (1957).

(13) W. D. Hobey and A. D. MacLachlan, *J. Chem. Phys.*, **33**, 1695 (1960). A very lucid description of the static and dynamic aspects of the Jahn-Teller effect is contained in this paper.

(14) See, for example, E. S. Pysh, J. Jortner, and S. A. Rice, *J. Chem. Phys.*, **40**, 2018 (1964).

(15) E. A. LaLancette and R. E. Benson, to be published.

The resonance energy of $C_9H_9^-$ is also of theoretical interest. If we choose the cyclononatetraene anion with noninteracting double bonds and fixed charge as



references state and further neglect compression energy considerations, the Hückel resonance energy of $C_9H_9^-$ is 3.516β , compared to 2.000β for benzene. Thus, the stabilization energy per π -electron is 0.35β , slightly greater than that of benzene, 0.33β .

A more realistic estimate can be obtained from ASMO theory employing a real Hamiltonian. The results for benzene and cyclononatetraenide are given in Table IV. The energy of N π -electrons before bond

Table IV. Energy Terms for C_6H_6 and $C_9H_9^-$

	$C_6H_6^a$	$C_9H_9^-$
H°	-171.465	-301.596
$H^\circ + NI_c$	-102.201	-186.156
E^{f+}	+87.327	+173.022
E^π	-84.138	-128.574
E_b	-14.874	-13.134
E^π/N	-14.023	-12.857
E_b/N	-2.479	-1.313

^a All energies are given in e.v.

formation is $-NI_c$, where I_c is the appropriate valence-state ionization potential. The repulsion energy in the σ -framework due to the positive charges in the core in this model can be written

$$E^{f+} = \sum_{p < q} [pp|qq]$$

where $[pp|qq]$ is the two-center Coulomb repulsion integral over AO's. Ruedenberg¹⁶ has defined the effective π -energy of the conjugated system as

$$E^\pi = H^\circ + E^{f+}$$

and the effective bonding energy of π -electrons relative to the carbon valence state as

$$E_b = E^\pi + NI_c$$

H° is the calculated π -electron energy of the ground state.

It is seen from the table that the π -energy of the system per electron (E^π/N) and the bonding energy of π -electrons relative to the valence state per electron (E_b/N) is larger in benzene than in cyclononatetraenide. Hence, when electron repulsion effects are included, MO theory predicts that stabilization gained by π -electron delocalization is considerably less in $C_9H_9^-$ than in C_6H_6 . This conclusion is at variance with simple Hückel theory and warns once again that energy terms cannot be adequately treated in general by theories not specifying the energy operator. Furthermore, the σ -framework orbitals are probably bent in $C_9H_9^-$ with a concurrent loss in stability relative to C_6H_6 , although this factor may not be as large as commonly supposed.¹⁷

(16) K. Ruedenberg, *J. Chem. Phys.*, **34**, 1861 (1961).

(17) H. E. Simmons and J. K. Williams, *J. Am. Chem. Soc.*, **86**, 3222 (1964).