Molecular Orbital Treatment of Tropolone(1)

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In the previous paper(2) we measured the dipole moment of tropolone (cycloheptatriene-2, 4, 6-ol-2-one-1) and its derivatives(3) and discussed the molecular structure of these compounds. We arrived at the conclusion that these molecules resonate among various electronic structures contributing to the normal states of these molecules and that each bond in the ring has a certain amount of double bond character causing plane cycloheptatrienolone ring. We found that the dipole moments of tropolone and hinokitiol (4-isopropyl-cycloheptatriene-2, 4, 6-ol-2-one-1) are nearly pointing along the line from the center of the ring to the middle point of two O-atoms with a positive end at the ring. The positions of substituents in the substituted tropolone and hinokitiols were determined, though for a few of them two alternatives were given to be decided finally by further investigations.

The theoretical investigations on the conjugated double bonds by the method of molecular orbitals have already been applied to the molecules of various compounds and have succeeded in the elucidation of the geometrical structures of these molecules, dipole moments, resonance energies, absorption spectra, chemical reactivities, etc. In the present paper we wish to report the results of application of the method of molecular orbitals to tropolone and show

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(1) Presented at the General Discussion on Structural Chemistry held by the Chemical Society of Japan on 8 July 1950.

(2) Y. Kurita, T. Nozoe and M. Kubo, this Bulletin, **24**, 10 (1951).

(3) T. Nozoe *et al.*, *Proc. Japan Acad.*, **26**, No. 7, 38, 43, 47 (1950).

that the results obtained experimentally are reasonably correct from theoretical considerations. Finally we shall give the characteristic properties of cycloheptatriene ring.

In the LCAO-molecular orbital method, each electron is considered to be in the self-consistent field due to other electrons and atomic nuclei and the single electron wave function ψ_j is approximated by a linear combination of atomic orbitals φ_k, each belonging to one of the nuclei. We treat the problem as a π-electron system, excluding, for a while, σ-electrons involved in the formation of single bonds.

$$\psi_j = \sum_k a_{jk}\varphi_k$$

The electronic energy E_j of the molecular orbital ψ_j can be obtained as roots $E=E_j$ $(j=1, 2, .. l)$ of a secular equation,

$$D = |H_{mk} - S_{mk}E| = 0,$$

where l denotes the number of π-electron atomic orbitals and H_{mk} and S_{mk} are given by the following equations respectively.

$$H_{mk} = \int \varphi_m{}^* H \varphi_k d\tau, \quad S_{mk} = \int \varphi_m{}^* \varphi_k d\tau.$$

The coefficients a_{jk} can be calculated by solving a set of simultaneous equations,

$$\sum_{k=1}^{l} a_{jk}(H_{mk} - S_{mk}E_j) = 0, \quad j, m = 1, 2 .. l,$$

and normalizing the wave function ψ_j. The wave function for the ground state can be obtained if we allot all π-electrons successively to the molecular orbitals ψ_j of low energy E_j, with the restriction that only two electrons of opposite spin can be adopted by each orbital.

An electron in the molecular orbital ψ spends a fraction $a_{jk}{}^2$ of time in the atomic orbital φ_k. Consequently the mean number of π-electrons at k-atom is given by

$$q_k = \sum_j |a_{jk}|^2,$$

where the sum extends over all molecular orbitals ψ_j occupied by electrons in the ground state. The bond order p_{lm} was defined by Coulson⁽⁴⁾ as

$$p_{lm} = \sum_j a_{jl}a_{jm}.$$

The sum of bond orders relating to l-atom, *i. e.*,

$$N_l = \sum_m p_{lm}$$

expresses the saturation degree of valency of l-atom. Coulson⁽⁵⁾ defined the free valence index of l-atom by

$$F_l = N_{\max} - N_l$$

and gave to $N_{\max}$ (the maximum value of N_l) the value of 1.68 for carbon. The free valence index is a measure of reactivity of the atom towards a free radical. The constitutional formula with the inscription of values of q_k, p_{lm} and F_l is called a molecular diagram.⁽⁶⁾

In actual calculation for a molecule under investigation, we make the approximation that H_{mk} is zero except Coulomb integrals H_{kk} and exchange integrals between neighboring atoms, since exchange integrals will decrease rather rapidly as the distance between the atoms increases. In a similar manner, as for the matrix components of unity, the overlap integrals are assumed to be $S_{mk}=0$, while $S_{kk}=1$. We now introduce, for the convenience of calculation, two quantities δ_k and ρ_{mk} defined by⁽⁷⁾

$$H_{kk} = \alpha_k = \alpha + \delta_k\beta, \quad H_{mk} = \beta_{mk} = \rho_{mk}\beta,$$

where α is the Coulomb integral of an electron in a π-orbital of benzene molecule, and β is the exchange integral between neighboring C-atoms in the same molecule.

The calculation of successive approximation must be carried out until the final result is self-consistent.⁽⁸⁾ First a set of proper values is chosen for δ_k and ρ_{mk}, *i.e.*, for α_k and β_{mk}. These enable us to calculate molecular orbitals, which in turn give q_k and p_{mk}. The total charge Q_k of each atom in the molecule and the interatomic distance r_{mk} between neighboring atoms can be obtained from q_k and p_{mk} respectively. Then α_k and β_{mk} are calculated from Q_k and r_{mk} respectively. The calculated values will not in general be identical with the original set. The calculations are repeated with the new set. This procedure is continued until the assumed set and the calculated set are almost identical. Four functional relations between q_k and Q_k, Q_k and α_k, r_{mk} and β_{mk}, p_{mk} and r_{mk} are required for the calculation. We used the following interrelations. (i) The total charge Q_k belonging to each atom is

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(4) C. A. Coulson, *Proc. Roy. Soc.* (London), A, **169**, 423 (1939).

(5) C. A. Coulson, *Chem. Abstr.*, **43**, 6877 (1949).

(6) A. Pullman, B. Pullman and P. Rumpf, *Bull. soc. chim. France*, **1948**, 757. B. Pullman and G. Berthier, *ibid.*, **1948**, 788.

(7) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).

(8) G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949).

equal to the sum of the nuclear charge, the charge of electrons in an inner shell, π-electron density q_k and σ-electron density, which is given by $\sum(l)\,\mu_{kl}/r_{kl}$, where μ_{kl} and r_{kl} denote respectively the dipole moment of σ-bond and interatomic distance between k- and l-atom. The sum is over all σ-bonds attached to the k-atom. (ii) According to Sandorfy,(9) α_k is proportional to the electronegativity χ_k of an atom. Assuming $\alpha/\beta=4.1$, the values of δ_k are calculated as shown in Table 1. For an atom with a charge Q_k correction term must be added. According to Pauling(10) a unit positive formal charge increases the electronegativity of an atom by an amount approximately equal to two-thirds of the difference between the electronegativities of that atom and the next atom to the right in the periodic table, and a negative formal charge similarly decreases the electronegativity value. Hence for an a-atom with a charge Q_k, the electronegativity χ_k is given by

Table 1

Electronegativity χ_k and δ_k

Atom	χ_k	δ_k
C	2.50	0.00
N	3.15	1.07
O	3.60	1.80
F	4.15	2.70

$$\chi_k = \chi_a + \frac{2}{3}(\chi_b - \chi_a)Q_k,$$

where χ_b denotes the electronegativity of a b-atom, the right neighbor of the a-atom. From the proportionality of electronegativity and Coulomb integral, $\alpha_k=(\chi_k/\chi_C)\alpha_C=\alpha_C+(\chi_k/\chi_C-1)\alpha_C$, and by definition, $\alpha_k=\alpha_C+\delta_k\beta$. Hence

$$\delta_k = \left(\frac{\chi_k}{\chi_C}-1\right)\frac{\alpha_C}{\beta}$$

Inserting in this equation the value of χ_k obtained above,

$$\delta_k=\left[\left(\frac{\chi_a}{\chi_C}-1\right)+\frac{2}{3}\left\{\left(\frac{\chi_b}{\chi_C}-1\right)-\left(\frac{\chi_a}{\chi_C}-1\right)\right\}Q_k\right]\frac{\alpha_C}{\beta}=\delta_a+\frac{2}{3}(\delta_b-\delta_a)Q_k.$$

Hence for carbon

$$\delta_k = \frac{2}{3}\delta_N Q_k = 0.71Q_k,^{(11)}$$

and similarly for oxygen

$$\delta_k=1.80+\frac{2}{3}(\delta_F-\delta_O)\,Q_k=1.80+0.60Q_k,$$

$$\delta_k=1.80+\frac{2}{3}(\delta_O-\delta_N)\,Q_k=1.80+0.49Q_k,$$

for $Q_k>0$ and $Q_k<0$ respectively. Considering the polarization of σ-bonds, the value of δ for a C-atom neighboring to a hetero-atom was assumed to be equal to one-tenth of δ of the latter atom. (iii) The exchange integral β_{mk} was assumed by Sandorfy(9) to be inversely proportional to the fourth power of interatomic distance r_{mk}. (iv) The relation between the bond order p_{mk} and interatomic distance r_{mk} is given by Coulson's curve(4) for C-C bonds. We calculated the bond order of C-O bonds for various compounds as shown in Table 2. Approximately linear relation is obtained between the bond order and the interatomic distance.

Table 2

Interatomic Distance and Bond Order of C-O Bonds

	Interatomic distance	Bond order
Single bond	1.43	0
Resorcine	1.36	0.28
$CaCO_3$	1.31	0.58
$NaHCO_3$	1.27	0.68
Double bond	1.22	0.94
Double bond*	1.185	1

* Ideal double bond with no ionic character(12)

Molecular Diagram of Tropolone.—The C-atoms of tropolone are numbered in the same way as the nomenclature "cycloheptatriene-2, 4, 6-ol-2-one-1." Let us call the two O-atoms attached to the position 1 and 2 respectively by the number 8 and 9. Molecular orbitals are constructed from π-orbitals belonging to these nine atoms. The number of electrons to be put in these orbitals is ten, *i. e.*, eight electrons for double bonds plus two electrons for a lone pair at one of the O-atoms. Though the two O-atoms are not exactly equivalent, they are supposed to be nearly so, owing to the hydrogen bond formation and resonance. Therefore we assign to each of them a charge of $+1.5\,e$ for the sum of the charge of a nucleus and electrons in an inner shell and a charge $-0.12\,e$ due to the

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(9) C. Sandorfy, *Bull. soc. chim. France*, **1949**, 615.

(10) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York (1948), p. 66.

(11) Wheland and Mann(8), in calculating the dipole moment of fulvene, assumed the coefficient to be equal to 1 instead of 0.71.

(12) R. Cantarel, *Bull. soc. chim. France*, **1949**, M 327.

polarization of O-H σ-bond. Consequently the molecule is assumed to be symmetrical across a plane through C-atom 5 and the middle point of C-atoms 1 and 2, and perpendicular to the ring. As a zeroth approximation we put $\rho_{mk}=1$, $\delta_8=\delta_9=2$ and $\delta_k=0$ for C-atoms. Calculation gives for the dipole moment due to π-electrons the value of $\mu_\pi=8.7\,\text{D}$. The first and the second approximations give 6.7 D and 4.4 D respectively. The molecular orbitals for the last calculation in the order of increasing energy are found to be

$$\begin{aligned}\psi_S(-2.773)=&0.442(\varphi_9+\varphi_8)\\&+0.489(\varphi_2+\varphi_1)+0.222(\varphi_3+\varphi_7)\\&+0.114(\varphi_4+\varphi_6)+0.084\varphi_5,\\ \psi_A(-2.131)=&0.574(\varphi_9-\varphi_8)\\&+0.338(\varphi_2-\varphi_1)+0.213(\varphi_3-\varphi_7)\\&+0.104(\varphi_4-\varphi_6),\\ \psi_S(-1.765)=&0.224(\varphi_9+\varphi_8)\\&+0.066(\varphi_2+\varphi_1)-0.241(\varphi_3+\varphi_7)\\&-0.479(\varphi_4+\varphi_6)-0.562\varphi_5,\\ \psi_A(-1.137)=&-0.289(\varphi_9-\varphi_8)\\&+0.061(\varphi_2-\varphi_1)+0.465(\varphi_3-\varphi_7)\\&+0.444(\varphi_4-\varphi_6),\\ \psi_S(-0.572)=&0.437(\varphi_9+\varphi_8)\\&-0.292(\varphi_2+\varphi_1)-0.359(\varphi_3+\varphi_7)\\&+0.105(\varphi_4+\varphi_6)+0.409\varphi_5,\end{aligned}$$

where the suffixes S and A donote the symmetry properties of the wave functions, and the number in the parentheses give $y_j=(\alpha-E_j)/\beta$,(13) instead of E_j. The results for the ground state,

$$\psi_S^2(-2.773)\psi_A^2(-2.131)\psi_S^2(-1.765)\\ \times\psi_A^2(-1.137)\psi_S^2(-0.572)$$

are given in the molecular diagram depicted in Fig. 1.

The direction and the magnitude of the dipole moment of tropolone have been determined in the previous paper(2) and is shown in Fig. 2. The π-moment can be obtained by

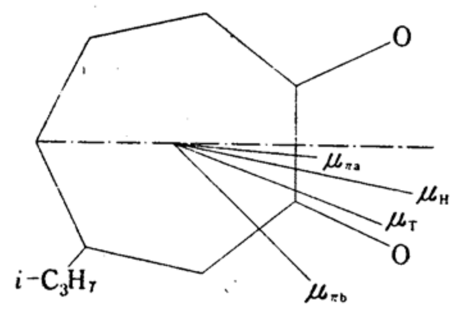
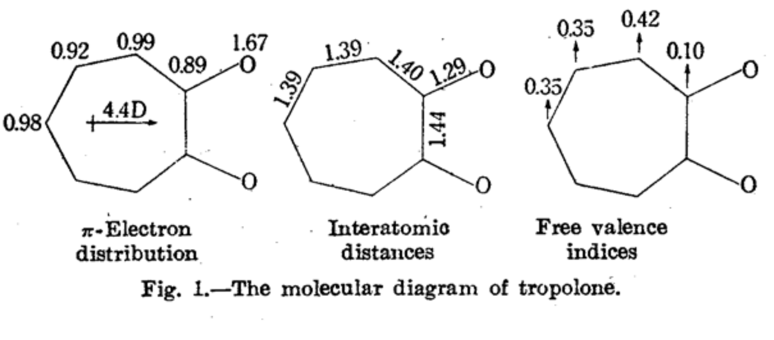


Fig. 2.—Dipole moment of tropolone: $\mu_H=4.04\,\text{D}$, hinokitiol; $\mu_T=3.7\,\text{D}$, tropolone; $\mu_{\pi a}=2.4\,\text{D}$, $\mu_{\pi b}=3.3\,\text{D}$, π-moment of tropolone.

subtracting two C-O bond moments (μ(C-O) = 0.86 D), one O-H bond moment (μ(O-H) = 1.53 D), and five C-H bond moments (μ(C-H) = 0.40 D). The results is $\mu_{\pi a}=2.4\,\text{D}$ if hinokitiol is 4-isopropylcycloheptatriene-2, 4, 6-ol-2-one-1, or $\mu_{\pi b}=3.3\,\text{D}$ if the compound is isopropylcycloheptatrienol-1-one-2. The direction of the dipole moment $\mu_{\pi a}$ thus obtained is nealy coincident with the result of molecular orbital treatment. As regards its magnitude, the calculated value is still greater than the observed one. Further approximation will be necessary to reach perfect agreement.

All C-atoms in the ring have a mean number of π-electrons less than unity, indicating that π-electrons are displaced from the ring. The π-electron distribution suggests that electrophilic atoms and radicals will attack the C-atoms 7 (ortho'(14)), 3 (ortho) and 5 (para), the former two being more liable to be attacked than the latter. This justifies our assumption made in the previous paper that only C-atoms 7, 3 and 5 are to be considered for the position



π-Electron distribution   Interatomic distances   Free valence indices

Fig. 1.—The molecular diagram of tropolone.

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[13] Since β is negative, the lower the energy E_j is, the smaller the value of y_j.

[14] T. Nozoe, *Yakugaku*, 3, 174 (1949).

of substituents such as a Br-atom or a nitro-group and that α-monobromohinokitiol is 7-bromohinokitiol.(15) The free valence indices indicate that reagents of free radical type will react at C-atoms 7 and 3.

The total energy is found to be $10\,\alpha + 16.756\,\beta$, while that of the electronic state represented by an ordinary constitutional formula without taking into account the resonance effect is $10\,\alpha + 13.664\,\beta$. Hence resonance energy is $3.09\,\beta$, as compared with $2\,\beta$ for benzene. This accounts for the aromatic character of tropolone-type molecules.

As has already been mentioned, it is almost certain from the theoretical considerations as well as from experimental results that in tropolone and its derivatives electrons are displaced away from the ring. It seems very probable that the same effect occurs in the case of other compounds with cycloheptatriene ring. In fact, Berthier and Pullman(16) have carried out molecular orbital treatment on methylene-cycloheptatriene and calculated its dipole moment to be equal to 2.35 D with the positive end at the ring. It seems appropriate to mention in this connection that they studied also fulvene with a cyclopentadiene ring, and found a moment of 3 D with the negative end at the ring. In fact, these tendencies reveal themselves in condensed rings as well as in the case of hyperconjugation. The characteristic electron distribution seems to be the cause of the peculiar properties of tropolone-type compounds in general.

Summary

The molecular orbital treatment was carried out on tropolone. The π-electron distribution, interatomic distances, free valence indices and dipole moment were derived. It was found that the dipole moment is very high (second approximation value of π-electron moment = 4.4 D) owing to resonance and lies along a line from the center of the ring to the middle point between two O-atoms with its positive end at the ring and that the resonance energy amounts to about 1.5 times that of benzene in general agreement with experimental results. It was shown that the substitution by electrophilic atoms and groups are most liable to occur at C-atoms 7, 3 and 5.

We wish to express our thanks to Prof. T. Nozoe of Tohoku University for his interest on this subject and many valuable discussions from organic chemical point of view. Our thanks are also due to the Ministry of Education in aid of this research.

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(15) The position 3 (ortho) will be more difficult to be attacked than 7 (ortho′) owing to steric effect.

(16) G. Berthier and B. Pullman, *Bull. soc, chim. France*, 1949, D 457.