THE GROUND STATE PROPERTIES OF

1,2,3,4-TETRACHLORO-5,6-DIPHENYLCALICENE

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In the previous paper (1) we have reported the synthesis
and some properties of 1,2,3,4-tetrachloro-5,6-diphenylcalicene
(I).

Theoretical considerations (2) have predicted that the
calicene system (II) would have a stable closed-shell electronic
configuration and that the dipolar resonance structure (IIa)
would make an unusually large contribution to its ground state
due to a charge transfer from the electron-donating three-
membered ring towards the electron-accepting five-membered ring.
Very recently, however, Dewar and Gleicher (3) have reported the
calculations for calicene and its benzo derivatives by the semi-

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empirical SCF MO procedures and have concluded that calicene is
not aromatic molecule.        Several significant contributions
concerning the synthesis and the polar nature of the calicene
system (1, 4 - 9) have appeared recently.



(I)                        (II)                      (IIa)
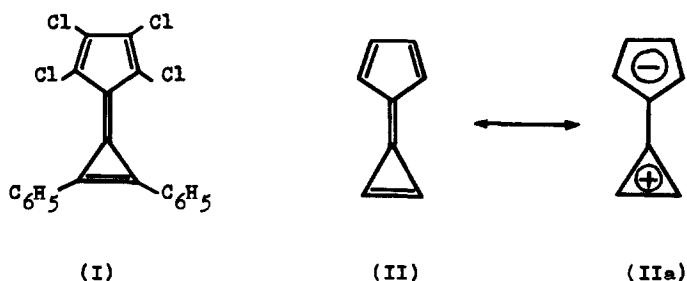
We now wish to report, in preliminary form, some ground
state properties for our compound (I) which is suitable for
theoretical verification of dipole moment.

The experimental fact that the dipole moment of (I) is
7.97 D in benzene at 25°C (10) indicates that the dipolar
structure is a major contributor to the resonance hybrid.

In using the LCAO MO theory we need to employ the bond
alternation technique (11) [bond alternation parameter :
$k = \beta_{single}/\beta_{double} = 0.59$ for calicene skeleton (12) and for
bonds 6 - 9, 5 - 15 and all $\beta$'s equal to 0.80 for two phenyl
groups], because only a single unexcited Kekulé structure can
be written for this molecule.      Assuming the entire molecule
to be coplanar, the orbital energies, pi-electron densities,

bond orders, bond lengths and free valencies were obtained for carbon skeleton (III) of (I), and are summarized in Table-1. The numbering of (III) is shown in Fig - 1.   The bond lengths, $r_{ij}$, were calculated with the aid of the formula (11),

TABLE - 1   (14)

| Bonding MO | Energy | Atom | Charge Density | Free Valence | Bond | Bond Order | Bond Length |
|---|---|---|---|---|---|---|---|
| 1 | 1.92813 | 1 | 1.03524 | 0.47891 | 1-2 | 0.88636 | 1.352 |
| 2 | 1.62400 | 2 | 1.06796 | 0.43065 | 2-3 | 0.41504 | 1.443 |
| 3 | 1.61767 | 5 | 0.89927 | 0.22362 | 1-8 | 0.36678 | 1.452 |
| 4 | 1.39418 | 7 | 0.83975 | 0.13782 | 7-8 | 0.77995 | 1.375 |
| 5 | 0.86278 | 8 | 1.17919 | 0.21844 | 5-7 | 0.40714 | 1.444 |
| 6 | 0.82545 | 9 | 1.00550 | 0.16911 | 5-6 | 0.81427 | 1.369 |
| 7 | 0.80000 | 10 | 0.99344 | 0.42126 | 6-9 | 0.28702 | 1.467 |
| 8 | 0.80000 | 11 | 1.00032 | 0.39668 | 9-10 | 0.63796 | 1.402 |
| 9 | 0.74760 | 12 | 0.99504 | 0.40697 | 10-11 | 0.67283 | 1.395 |
| 10 | 0.44783 | | | | 11-12 | 0.66254 | 1.397 |



(III)
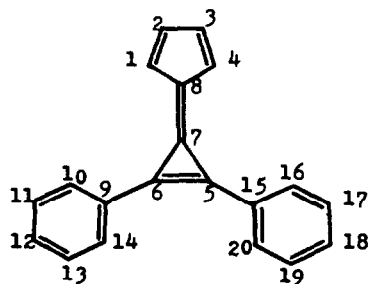
Fig - 1

$r_{ij}(\text{Å}) = 1.520 - 0.186 \, p_{ij}$, in which $p_{ij}$ designates the computed bond order between atoms i and j.      From the above data we obtained the theoretical dipole moment of 5.73 D for (III).

It is difficult to estimate the effect of the four chlorine atoms for the dipole moment of this system, but if we follow the assumption in our previous paper (15), this effect is assumed to be 1.1 D in the same direction as in (III) and the theoretical dipole moment of (I) should be 6.83 D.      Nevertheless, if we use the value of 1.53 D, instead of 1.1 D, which is difference between the observed moment of 1,2,3,4-tetrachloro-6-phenyl-fulvene [2.63 D] and of 6-phenylfulvene [1.10 D], for this effect the theoretical dipole moment of (I) should be 7.26 D.      This latter value is in fairly good agreement with the observed value [7.97 D].

It is a significant feature that the bond order between each pair of rings is 0.780 which is in good agreement with those of sesquifulvalene [0.776] (16) and benzo[g] sesquifulvalene [0.786] (17).      The value [0.780] is much less than the bond orders of pinched bonds in fulvalene [0.846] (11) and hepta-fulvalene [0.823] (11).      This means that (III) has more single bond character than the latter molecules.

When the four chlorine atoms were included in the MO calculations by using the parameter $\alpha_{Cl} = \alpha_o + 2.0\beta_o$, $\beta_{C-Cl} = 0.4\beta_o$ (18), the theoretical dipole moment was found to be 5.99 D.

The basicity of (I) was determined by examining the ultra-violet absorption spectrum as a function of $H_o$ of the solvent,

aqueous sulfuric acid.    The pK of (I) is ca. -4.7 which is
comparable to that of 2,4-dinitroaniline [-4.35] (19) but less
than those of 2,3-dibenzoyl-5,6-dipropylcalicene [-2.0] (5) and
diphenylcyclopropenone [-2.5] (20).

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$$V = E_\pi + E_\sigma = (2/ab)\sum_{i<j}\beta_{1j} + \sum_{i} q_1\alpha_1 + Const. \qquad (13)$$

    with a series of k values varying from 0 to 1, and the
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