CROATICA CHEMICA ACTA **37** (1965) 307

CCA-388

543.862.2.02
Note

Molecular Orbital Calculations for [18] Annulene Trioxide

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Received September 15, 1965

Recently[1], the synthesis of [18] annulene trioxide has been reported, the atomic skeletal structure of which is shown in Fig. 1. [18] annulene trioxide is one member of a series of related compounds which has recently been synthesized[1,2,3]. The most closely related compounds are [18] annulene trisulphide and [18] annulene oxide disulphide. It has been found that the chemical properties of [18] annulene trioxide are very similar to those of [18] annulene trisulphide[1]. On the other hand, experimental[3] and theoretical[4] results indicate that [18] annulene trisulphide has considerably less aromatic character than [18] annulene, and that it can be considered as being composed of three thiophene rings linked together by three double bonds. It is therefore of interest to examine whether theoretical calculations for [18] annulene trioxide favour a fully conjugated

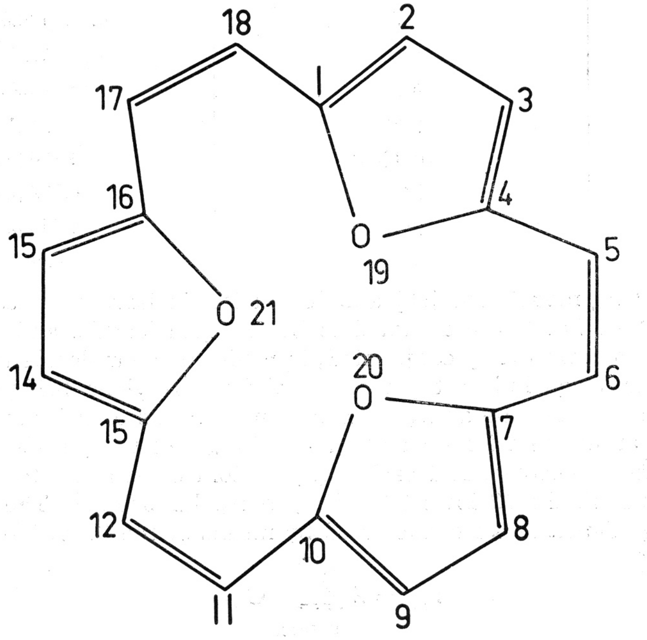

Figure 1. [18] Annulene Trioxide

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model or rather a model which can be considered as a system of essentially non-conjugated furan rings.

In this paper we examine this problem and report the Hückel molecular orbital [HMO][5] calculations for [18] annulene trioxide.

Due to the steric requirements of the sulphur atoms, [18] annulene trisulphide is a non-planar molecule[3]. Whilst it is possible to assume that [18] annulene trioxide is also non-planar (supported by the similarities in the chemical properties of these two compounds) it is also possible for [18] annulene trioxide to exist as a planar molecule because of the considerably lower steric requirements of the oxygen atoms. (Planar [18] annulene trisulphide would be more highly strained than planar [18] annulene trioxide.)

We started our calculations using a standard choice of parameters for the heteroatoms (recommended by Streitwieser[6])

$$\alpha_x = \alpha_c + h_x\beta_{cc}$$
$$\beta_{cx} = k_{cx}\beta_{cc}$$

where h_x and k_{cx} are dimensionless parameters for a particular heteroatom in a given molecular environment. The values of α_x and β_{cx} are given in Table 1.

TABLE I.

Coulomb and Resonance Integrals

	I	II
α_1	α_C	α_C*
α_X	$\alpha_C + 1.720\beta_{CC}$	$\alpha_C + 1.720\ \beta_{CC}$*
α_2	α_C	$\alpha_C - 0.040\ \beta_{CC}$*
α_5	α_C	$\alpha_C + 0.020\ \beta_{CC}$*
β_{12}	β_{CC}	β_{CC}*
β_{1X}	$0.760\ \beta_{CC}$	$0.760\ \beta_{CC}$*
β_{23}	β_{CC}	$0.592\ \beta_{CC}$*
β_{45}	β_{CC}	$0.540\ \beta_{CC}$
β_{56}	β_{CC}	$1.020\ \beta_{CC}$

Two (planar) models for [18] annulene trioxide have been considered: in model I all C—C bonds are assumed to be of equal lengths and the annulene ring may be considered fully conjugated; in model II the molecule is represented by three furan rings linked together by olefinic vinylene bridges. For these models we will discuss the aromatic character in terms of the bond orders.

The [18] annulene trioxide system has 24 π-electrons, each carbon atom contributes one π-electron, and each oxygen atom contributes two π-electrons. These electrons fill the 12 lowest bonding molecular orbitals. The bond orders and the charge densities were calculated by means of the following expressions:

$$P_{\mu\mu} = 2 \sum_{r\ \mathrm{occ.}} C^2_{r\mu}$$

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* (A Similar choice of parameters has been given by Sappenfield and Kreevoy[7] for furan)

$$P_{\mu\nu} = 2 \sum_{r\ \mathrm{occ.}} C_{r\mu}\, C_{r\nu}$$

which were introduced and defined by Coulson[8].

The calculated bond orders and charge densities are shown in Tables II. and III. In both models the calculated bond orders show that the $C_5 - C_6$ bond has more double bond character than the others. If we use the following formula[9]:

$$l = 1.517 - 0.180\ P_{\mu\nu}$$

where l is the calculated bond length in angstroms, we obtain the following C_5-C_6 bond lengths for the two cases: model I — 1.390 Å and model II — 1.350 Å (see Table IV). This result favours model II as being the more suitable structure for [18] annulene trioxide. The chemical evidence suggests that the C_5-C_6 bond is olefinic and one should expect the experimental C_5-C_6 bond length to be somewhere between 1.35—1.37 Å.

TABLE II.
Bond Orders

Bond	I	II	[18] annulene trisulphide* [4]
$C_1 - C_2$	0.634	0.848	0.630
$C_1 - X$	0.332	0.334	0.368
$C_2 - C_3$	0.654	0.418	0.658
$C_4 - C_5$	0.562	0.261	0.548
$C_5 - C_6$	0.703	0.931	0.715

TABLE III.
Charge Densities

Atom	I	II
C_1	1.002	1.000
C_2	1.056	1.086
C_3	1.032	1.007
O	1.822	1.814

TABLE IV.
Calculated Bond Lengths in Å

Bond	I	II
$C_1 - C_2$	1.403	1.364
$C_1 - X$	1.457	1.455
$C_2 - C_3$	1.399	1.442
$C_4 - C_5$	1.416	1.470
$C_5 - C_6$	1.390	1.350

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* (Case III in Ref. 4 with all α_C equal, $\alpha_X = \alpha_C + 1.5\ \beta_{CC}$, and $\beta_{CX} = 0.8\ \beta_{CC}$)

Model I also gives slight bond alternations; these are similar in magnitude to changes found in naphtalene and other fully aromatic systems. The important result, however, is that [18] annulene trioxide is less aromatic than [18] annulene, which consists of a planar ring and obeys "Hückel's rule", containing a closed-shell $(4n + 2)$ π-electrons (with $n = 4$). It is very important to understand the meaning of *aromaticity* and not to confuse it with *stability*. Cyclic unsaturated molecules having $(4n + 2)$ π-electrons will have a closed-shell configuration, and therefore will be chemically stable.* But the valid criteria for aromaticity are: a lower energy than would be predicted for the analogous system with fixed double bonds, the ability to sustain an induced ring current of π-electrons and the presence of C-C bonds which are intermediate in length between a single and a double bond[10].

In the case of [18] annulene trioxide and [18] annulene trisulphide two *inner* adjacent hydrogen atoms are replaced by oxygen or sulphur respectively, thus changing considerably the aromatic character of the annulene ring. An interesting question arises: what are the relationships between the aromatic characters of [18] annulene, [18] annulene trisulphide and [18] annulene trioxide? The following relationships are predicted from their spectral data:

[18] annulene $>$ [18] annulene trioxide $>$ [18] annulene trisulphide

[18] annulene trioxide has an electronic spectrum very similar to that of tridehydro [18] annulene[11] which is considered to be an aromatic hydrocarbon (this has been demonstrated, for example, from its NMR spectrum[11]). The electronic spectrum of [18] annulene trisulphide[2], however, supports the experimental and theoretical evidence that it has three thiophene rings and three double bonds linked together. The above relationships are also supported by an increasing double-bond character in the C_5-C_6 bond going from [18] annulene to [18] annulene trioxide and [18] annulene trisulphide.

The charge densities show slight π-electron migrations from the oxygen atoms into the carbon ring system.

The delocalisation energy of [18] annulene trioxide has been calculated by subtracting the HMO π-energy of the three isolated ethylene and three furan molecules from the total HMO π-energy of [18] annulene trioxide. The total π-energy of ethylene has been taken to be $E = 2\alpha + 2\beta$. The total π-energy of furan has been calculated for model I to be $E = 6\alpha + 8.57\beta$, and for model II $E = 6\alpha + 8.10\beta$. The delocalisation energy for model I is 3.19β, and for model II $1.09\ \beta$. The total HMO π-energies for both models are given in Table V.

TABLE V.
Total HMO π-Energies

	I	II
E	$24\alpha + 34.90\beta$	$24\alpha + 31.39\beta$

Acknowledgements. I would like to thank Prof. J. N. Murrell for helpful discussions and for making my stay at Sheffield University both possible and pleasant. I would also like to thank Dr. M. Randić for his interest in this work.

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* Free radicals will have $(4n + 1)$ π-electrons, and compounds with $(4n)$ π-electrons will have a triplet ground state.

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IZVOD

Račun molekularnih orbitala za [18] anulen trioksid

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Na osnovu indeksa (reda) veza izračunatih upotrebom Hückelovih molekularnih orbitala diskutira se aromatski karakter [18] anulen trioksida. Rezultat računa ukazuje, da je kod [18] anulen trioksida slabije izražen aromatski karakter, nego kod [18] anulena i da je veza C_5-C_6 slična dvostrukoj vezi, što je u skladu sa eksperimentalnim iskustvom. Ovaj rezultat potvrđuje relativan odnos obzirom na aromatičnost za [18] anulen, [18] anulen trioksid i [18] anulen trisulfid dobiven iz spektralnih podataka.

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Primljeno 15 rujna 1965.