276.   *Molecular-orbital Calculations for Clar's Hydrocarbon*
1 : 13 : 12-6 : 16 : 7-*Dibenzonaphthacene* (*Zethrene*).

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The carbon–carbon bond lengths of the polynuclear hydrocarbon
1 : 13 : 12-6 : 16 : 7-dibenzonaphthacene ($C_{24}H_{14}$; Clar's zethrene) have been
calculated by the simple molecular-orbital method.   There is some evidence
that the electronic structure differs from that of other polynuclear hydro-
carbons with six-membered rings (*e.g.*, naphthalene, ovalene) on account of a
low-lying π-electron orbital.   It is suggested that the reduction of zethrene
should lead first to a dihydrozethrene with a resonating framework related to
that of 1 : 1-dinaphthylethylene, despite the fact that Clar's experiments
with zinc dust or dithionite do not appear to confirm this.   Further
reduction, which leads experimentally to a chrysene derivative, can be
interpreted by a plausible theoretical scheme.   Calculations are also made of
the expected ultra-violet transitions among π-electron levels, and a tentative
interpretation is suggested for the three lowest energy bands.

RECENTLY Clar reported to us the synthesis of the hydrocarbon 1 : 13 : 12-6 : 16 : 7-di-
benzonaphthacene $C_{24}H_{14}$ (I), which has been called zethrene from its Z-like structure.
This hydrocarbon appears to have some properties that are rather unusual for polynuclear
hydrocarbons.

The extremely close agreement between the bond lengths predicted by the simple
molecular-orbital method for the polynuclear hydrocarbons ovalene (Buzeman, *Proc.
Phys. Soc.*, 1950, *A*, **63**, 827) and coronene and pyrene (Moffitt and Coulson, *ibid.*, 1948,
60, 309) and the bond lengths determined from the *X*-ray work of Robertson and his group
made it of interest to ascertain whether such close agreement would also be found for
zethrene.   The determination of the bond lengths of zethrene is at present under
investigation in the laboratories of Professor J. M. Robertson.   For that reason it seems
wise now to record the results of our calculations.

In addition to the calculations of the bond lengths, it seemed possible that the
theoretical calculations might throw light on some of the unusual properties of this
molecule.

In this paper we shall be concerned with : (1) a brief résumé of some of the properties
of zethrene;   (2) simple molecular-orbital calculations on the hydrocarbon;   (3) bond

lengths and free valences determined from these calculations; (4) the electronic structure of the first excited states of zethrene and a comparison with the observed spectra; (5) a consideration of the successive reduction products of zethrene. In a later paper we hope to discuss the Diels–Alder reaction of zethrene with maleic anhydride.

Properties of Zethrene.—A complete report on the chemistry of zethrene will be given elsewhere by Clar and his collaborators. But it will be desirable to present here a brief résumé of some of its unusual properties. In the first place, if the bond diagram of the molecule is written in the usual way, there are nine Kekulé structures of which (I) is an example. This is because the molecule could be thought of as two naphthalene nuclei A–B and E–F conjugated together across a central butadiene-like region, 5, 15, 18, 11. Each naphthalene nucleus possesses three such structures, and those associated with rings A–B are independent of those associated with E–F. But in all nine structures the central region preserves a butadiene-like character. In excited structures, of course, this fixation of the central bonds ceases to hold. Yet we may expect, by analogy with other molecules, that the main features presented by the Kekulé diagrams will be found in the complete molecular diagram. A somewhat similar situation occurs in perylene (II), where the two bonds joining the naphthalene nuclei always appear as single bonds in the nine Kekulé structures which may be drawn analogous to those of (I). The longer length of these " single " bonds in perylene has now been established experimentally. It will be interesting to see whether a similar disparity is (*a*) predicted and (*b*) observed for zethrene.

Despite the nine Kekulé structures such as (I), Clar feels that the unusual properties of zethrene are best expressed, not by (I), but by a classical equilibrium between molecules of types (I) and (III). In (III) the periphery of the carbon skeleton has a normal aromatic character, and encloses two localised π-electrons on carbon atoms 13 and 16. It is a little difficult to see any satisfactory wave-mechanical justification for this localisation. If we accept it, there are three Kekulé structures (III*a*, *b*, *c*) which can be drawn. We shall discuss this matter, and also two further ways in which the π-electron distribution may differ from that to be expected on conventional grounds.

(I)   (II)   (III*a*)   (III*b*)   (III*c*)
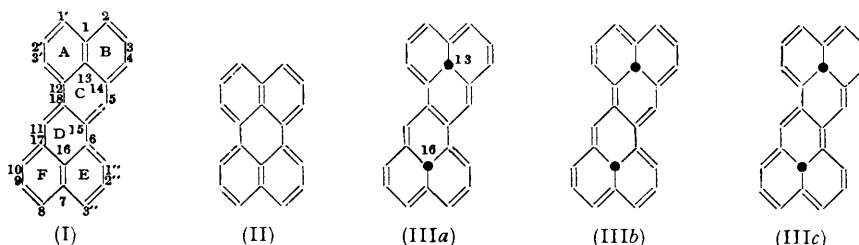
Zethrene is green and its visible and its ultra-violet spectrum exhibit no relation to any class of aromatic hydrocarbons previously examined. This is surprising, since as Clar has shown, there are very striking regularities among the ultra-violet spectra of almost all other polynuclear aromatic hydrocarbons. Zethrene is sparingly soluble in neutral solvents but is readily soluble in dilute acetic acid. The spectrum of the neutral solution of zethrene differs considerably from that of the hydrocarbon in acid solvents and in some respects is similar to the spectrum of the free radical acetoxyperinaphthenyl (IV). The structure of zethrene in acid is considered by Clar to be (V). Reduction of the violet acid solution with zinc dust or hydrosulphite (dithionite) yields a yellow compound which Clar believes to be (VII), and which is readily re-oxidised to zethrene by oxygen. The possible dihydrozethrene (VII) differs from (VI), which was obtained by an independent synthesis, though when sublimed from the solid state, or when boiled with acetic acid, (VII) appears to be converted into (VI). Further reduction of (VI) with hydrogen iodide leads to a hydrocarbon (VIII), identified by means of its ultra-violet spectrum as a derivative of chrysene.

Molecular-orbital Calculations.—The usual molecular-orbital calculations have been

carried out for zethrene. Since they follow lines similar to those already published (*loc. cit.*) for coronene and ovalene, they will not be described in detail. The chief difficulty arises from the fact that since the only effective symmetry is that due to inversion in the centre of the molecule, the secular determinant cannot be reduced below two twelfth-order factors. The expansion of these was checked by using two distinct methods of building up the complete determinant out of smaller groups of atoms.

(IV) (V) (VI) (VII) (VIII)
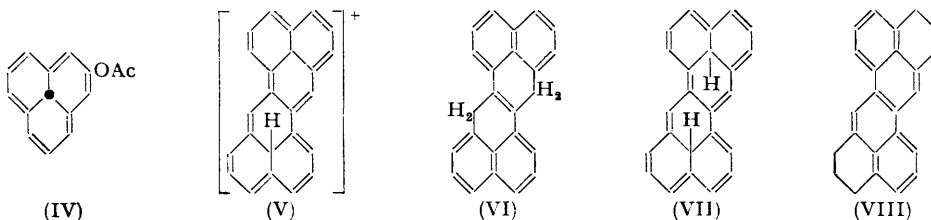
The roots of the secular equation give the energies of the various molecular orbitals, and the values for zethrene are listed in Table 1. The roots listed in the $k(\beta)$ column are the energies found with the simplest approximation, that is when overlap between adjacent atomic orbitals is neglected. The energies (following Coulson, *Proc. Phys. Soc.*, 1948, **60**, 257) are of the form :

$$E = E_0 + k\beta \qquad \qquad \qquad (1)$$

where E_0 is the energy of the $2p_z$ electron on any nucleus (for zethrene the z direction is taken to be perpendicular to the plane of the molecule), β is the resonance integral, and k

TABLE 1. *Energies of molecular orbitals of zethrene.*

Symmetry *	$k(\beta)$	$m(\gamma)$		Symmetry *	$k(\beta)$	$m(\gamma)$	
A	−2·590	−7·351		A	0·199	0·189	
S	−2·359	−5·748		S	0·776	0·650	
A	−1·901	−3·621		A	1	0·8	
S	−1·808	−3·299		S	1	0·8	
A	−1·683	−2·905		S	1	0·8	
S	−1·421	−2·204	Antibonding	A	1·163	0·901	Bonding
S	−1·163	−1·640		A	1·421	1·049	orbitals
S	−1	−1·333		S	1·683	1·185	
A	−1	−1·333		A	1·808	1·245	
A	−1	−1·333		S	1·901	1·288	
A	−0·776	−0·962		A	2·359	1·484	
S	−0·199	−0·209		S	2·590	1·572	

* The wave functions symmetrical about the centre of symmetry are labelled S, those anti-symmetrical about the centre of symmetry are labelled A. Correct group-theory designations are $S = a_u$, $A = b_g$.

is the numerical coefficient for each energy level found from the secular determinant. As Wheland (*J. Amer. Chem. Soc.*, 1941, **63**, 2025) has shown, the previously neglected overlap can easily be taken into consideration at this stage of the calculations. The energies of the orbitals (with overlap included) are now given by the equation :

$$E = E_0 + m\gamma \qquad \qquad \qquad (2)$$

where E_0 has its former meaning, $m = k/(1 + kS)$, $\gamma = \beta - S\alpha$, and $S = \int\phi_i\phi_j d\tau$ (*i* and *j* are neighbouring atoms). Where necessary S is given the numerical value of 0·25.

When the roots of the secular equation have been found, the coefficients for each atomic orbital in any molecular orbital can be readily determined (a list of these coefficients may be obtained on application to Dr. C. Moser). The molecular symmetry previously described compels the sets of coefficients to fall into two groups. In the first, called S, the coefficients for corresponding atoms (*e.g.*, 1 : 7 or 2 : 8) are equal : in the second, called A, they are equal and opposite. Eull group-theory designations are a_u and b_g respectively.

Once the coefficients of the molecular orbitals have been obtained, the bond orders p follow very quickly (Coulson, *Proc. Roy. Soc.*, 1939, *A*, **169**, 413). These mobile bond orders may be converted into bond lengths by the standard formula

$$x = s - \frac{s - d}{1 + K(1 - p)/p}$$

where s, d, x are the lengths, in Å, of a single bond, a double bond, and a bond of mobile order p, respectively, and K is a constant chosen so that the order–length curve passes

TABLE 2. *Bond orders and bond lengths in zethrene.*

Bond	Mobile bond order	Length (Å)	Length (Å) *	Bond	Mobile bond order	Length (Å)	Length (Å) *
1—2	0·550	1·416	1·416	12—13	0·540	1·418	1·417
1—13	0·527	1·420	1·420	12—18	0·425	1·440	1·437
1—1'	0·553	1·415	1·415	12—3'	0·628	1·401	1·411
2—3	0·694	1·388	1·396	13—14	0·510	1·423	1·425
3—4	0·645	1·398	1·391	15—18	0·466	1·432	1·411
4—14	0·601	1·406	1·420	1'—2'	0·701	1·389	1·393
5—14	0·513	1·422	1·408	2'—3'	0·637	1·400	1·394
5—15	0·692	1·390	1·412				

* These columns refer to a possible effect of configuration interaction. See p. 1345.

through the triple-bond point. This makes $K = 2(d - t)/(s - t)$, where t is the triple-bond length. The corresponding orders and lengths are shown in Table 2, columns 2, 3, 6, and 7. The basic lengths s, d, t have been taken equal to 1·540, 1·340, and 1·204 Å respectively. In view of our continuing ignorance of the true value of the double-bond length d, no absolute accuracy is expected for the third decimal in this table. But, as the example of ovalene suggests, relative validity may be much greater.

Since this molecule is an alternant hydrocarbon (Coulson and Longuet-Higgins, *ibid.*, 1947, *A*, **191**, 39), the charge distribution is uniform, to the approximation to which the method can be applied. But the free valences are not all equal (Burkitt, Coulson, and Longuet-Higgins, *Trans. Faraday Soc.*, 1951, **47**, 553). The free valence F_r at atom r is calculated from the formulæ

$$F_r = 1·414 - \sum_s p_{rs} \quad \text{if } r \text{ is a secondary carbon atom}$$

$$F_r = 1·732 - \sum_s p_{rs} \quad \text{if } r \text{ is a tertiary carbon atom}$$

Table 3 shows the values of F_r so obtained.

Bond Lengths and Free Valency.—The bond lengths reported in Table 2 suggest that the bonds most nearly double are those shown in (IX). The remaining bonds are all either (*a*) approximately equal to the normal aromatic length 1·39 Å, or (*b*) quite distinctly " single " in character. The bonds of type (*a*) are the remaining ones in the naphthalene nuclei, those of type (*b*) are the central ones. This means that the central part of the molecule resembles a butadiene system, as suggested above on the basis of Kekulé structures. We could say that there was a considerable degree of bond localisation in this region. The remaining " double " bonds in (IX) are the familiar 1 : 2-bonds of naphthalene. This shows, as is quite reasonable, that so far as possible, the naphthalene nuclei are not much distorted except where they are attached to the central " butadiene " system.

(IX)

As regards the free valence values, which would be expected to be significant in radical reactions, the most interesting figures are the high values at the atoms 5 and 11 which terminate the " butadiene " region, and the low values at the β-naphthalene positions 2' and 3. The significance of the high values at 5 and 11 will be brought out in our discussion of dihydrozethrene.

The value of F_{13} is of some importance since it allows us to discuss Clar's suggestion that zethrene should be represented as (III) as well as (I). If (III) were a completely adequate description, then (1) the bond orders in the whole of the perimeter should be more
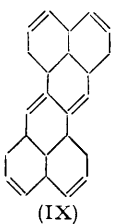
or less equal, and (2) the free valence at carbon atom 13 would be large. The first of these is certainly not the case, as we have seen (and we may hope for further verification of this when the experimental X-ray values for the bond lengths are available). The second is also not in accord with our calculations, which show that the free valence is effectively the same at positions 13 and 15 and not much greater than at position 12. This makes us feel that (III) is not a good representation of the electronic structure.

There is a further bond structure that might be considered as an alternative to (III). This is the lowest triplet state, in which there are two unpaired π-electrons. It differs from (III) in that in (III) the unpaired electrons are supposed to be strictly localised on atoms 13 and 16, whereas in the triplet state they will be distributed over the whole carbon skeleton. We shall consider this possibility in detail later.

The unusual properties of the ultra-violet spectrum and reduction of zethrene lead us to look for some unusual property of its energy levels. There is one such. It will be seen from Table 1 that the top occupied level has energy $E = E_0 + k\beta$, where $k = 0 \cdot 199$. This is exceedingly low, much lower, for example, than in benzene ($1 \cdot 000$), naphthalene ($0 \cdot 618$), or benzanthracene ($0 \cdot 452$). It means that the energy difference between the lowest-energy configuration and the next higher one is only $2 \times 0 \cdot 199\beta = 0 \cdot 398\beta$. Three points follow from this. First on the assumption that the lowest configuration is indeed a good approximation to the true ground-state wave function, the excitation energy to the first excited state (an allowed transition, according to this view) would be much lower than usual. If such a low value is not found, it probably means that the lowest configuration is not a good enough approximation, and configuration interaction of the kind discussed by Coulson, Craig, and Jacobs (*Proc. Roy. Soc.*, 1951, *A*, **206**, 297) and by Coulson and Fischer (*Phil. Mag.*, 1949, **40**, 386) is more than usually important. This will have an effect on bond orders and bond lengths. Let us estimate it by making the rather extreme assumption that the two lowest configurations of similar symmetry (which correspond to configurations 1 and 4 in the article by Coulson and Fischer, *loc. cit.*) have equal weight. This almost certainly exaggerates the influence on bond lengths. The new bond lengths are shown in columns 4 and 8 of Table 2, under the heading of " configuration interaction." The most notable difference between columns 3 and 4 (and 7 and 8) lies in the smaller degree of bond fixation in columns 4 and 8, particularly in the " butadiene " region. Thus when the experimental lengths of the bonds are available, we may hope to have further information on this matter. Other changes than that of the bond 5–15 are within the reasonable precision of the whole scheme of calculation, according to Coulson, Daudel, and Robertson's analysis (*Proc. Roy. Soc.*, 1951, *A*, **207**, 306).

The second point which follows from the low value of k for the top occupied orbital is that the first excited triplet level, which arises from one electron each in the orbitals $k = +0 \cdot 199$, $k = -0 \cdot 199$, will be expected to have an unusually low energy. It is even conceivable that this energy might be as low as that of the lowest singlet state. In such an event, the molecule would behave very much as a diradical. It would be prohibitively difficult to make calculations *ab initio* to establish this situation. The present authors are inclined to believe that it would not happen. But it should mean that there was an unusually low-lying triplet state. Related to this would be the prediction that zethrene should show considerable thermal instability. We do not know of any evidence with regard to this.

The third point is that electrons in the two molecular orbitals for which $k = \pm 0 \cdot 199$ will behave in a manner rather similar to that of non-bonding electrons in zero-energy orbitals (Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265). The actual values of the atomic coefficients in these molecular orbitals show that the electrons are almost entirely localised on atoms 1′, 3′, 2, 4, 5, and their mirror images in the centre of the molecule. The significance of this in any electronic interpretation of the reactivity of zethrene has been discussed fully by Longuet-Higgins. And the fact that this electron is hardly at all to be found on atom 13 is a further argument against the electronic bond diagram (III).

We can now discuss the possibility mentioned earlier that the quantum-mechanical version of Clar's concept of a classical equilibrium between two types of zethrene is not that of an equilibrium between (I) and (III), which we have seen to be theoretically

improbable, but that between (I) and the lowest triplet state. This could conceivably occur if the triplet energy was sufficiently low. But we believe that such an interpretation is not correct, for the following reasons. First, on account of the complementary character of the singly-occupied orbitals $k = \pm 0.199$, in this triplet state the net distribution of π-electrons is the same as in the ground state. Second, the two most loosely bound electrons—the unpaired electrons of the triplet—have a distribution which, as stated earlier, is almost entirely localised on atoms 1', 3', 2, 4, 5, and their mirror images. Thus there would be nothing resembling free electrons on atoms 13 and 16 in the triplet state any more than in the singlet ground state. Thirdly, the free valence values, shown in Table 3,

TABLE 3. *Free valence* (F.V.) *in ground state and first-excited* (*triplet*) *state.*

Carbon nos.	1,7	2,8	3,9	4,10	5,11	6,12	13,16	14,17	15,18	1',3"	2',2"	3',1"
F.V. (ground)	0·102	0·170	0·075	0·168	0·210	0·139	0·155	0·108	0·150	0·160	0·076	0·149
F.V. (triplet)	0·098	0·210	0·078	0·168	0·192	0·162	0·154	0·078	0·156	0·188	0·078	0·174

show that the values for atoms 13 and 16 in the triplet state scarcely differ from their values in the singlet ground state, so that the arguments used for the latter apply equally for the former. For these reasons it appears improbable that the concept of a classical equilibrium can be justified in terms of the triplet state. And there is no other state of sufficiently low energy.

It is worth while to refer briefly to the electronic transitions which our simple theory predicts. It is well known that on account of its failure to take adequate account of varying spin multiplicity these predictions must be accepted with considerable reserve. If we make use of the energies given in Table 1, then the three lowest energy transitions among the π-electrons are as shown in Table 4. Additional transitions at shorter wavelengths can soon be written down. We have not done so because they are close together, and their resulting absorption bands would certainly overlap. Now the visible and near ultra-violet spectrum of zethrene has been determined by Clar (" Aromatische Kohlenwasserstoffe," Springer, Berlin, 2nd edn., 1952, p. 389). There are weak maxima (log ε ~3) at 622 and 573 mμ, followed by a strong band (log ε ~5) at 461 mμ, and another fairly strong band (log ε ~4) at 342 mμ. Whether or not we treat the two bands at 622 and

TABLE 4. $N \longrightarrow V$ *Transitions in zethrene.*

Transition	Description * of electron jump		Excitation energy (units of γ)	λ(mμ) †
$N \longrightarrow V_1$	$b_g \longrightarrow a_u$	Allowed	0·398	943
$N \longrightarrow V_2$	$a_u \longrightarrow a_u$	Forbidden	0·859	437
$N \longrightarrow V_3$	$b_g \longrightarrow a_u$	Allowed	1·009	372
$N \longrightarrow V_4$	$b_g \longrightarrow b_g$	Forbidden	1·151	326

* With usual selection rules $u \longrightarrow g$ and $g \longrightarrow u$ transitions are allowed, $u \longrightarrow u$ and $g \longrightarrow g$ are forbidden, as with atomic spectra.

† Excitation energies are calculated with $\gamma = 3.3$ ev.

523 mμ as corresponding to different vibrational quanta of one electronic transition (the difference is unusually large for this interpretation) there does not appear to be any way of correlating these with the predicted transitions, as given in Table 4. The only conclusion which we feel entitled to draw from this is that it provides further support for the tentative suggestion made earlier, that on account of the low-energy orbital, configuration interaction is more important for this molecule than for most others. If the first excited transition is correctly interpreted, there should be a triplet of much lower energy. So far as we know, no data are available with which to test this view.

Reduction of Zethrene.—We may now discuss the reduction of zethrene, which, according to Clar, is not to the expected (VI), but is rather to (VII). Free valence considerations would have suggested that (VI) was formed more readily than (VII), as we have already said. A similar conclusion is obtained on the basis of energy stability. To prove this, let us compare the loss of π-electron energy in the two processes : (1) (I $\longrightarrow$ VI) ; (2) (I $\dashrightarrow$ VII).

The first of these processes leads to a resonating framework which, as regards its π-electron structure, can be regarded as almost equivalent to 1 : 1-dinaphthylethylene. The values of the energies of the molecular orbitals of this system are available (Berthier, Berthod, Mayot, and Pullman, *Compt. rend.*, 1950, **231**, 1149), so that the total π-electron energy is soon found. The second process leads to a resonating framework which, as a first approximation, is shown in (X). For (X) purposes of calculating the energies of the orbitals, this is equivalent to a cyclic polyene of 22 atoms, with a bond along one diameter. The method of calculating the energies is quite straightforward and will not be described here. When the sets of energies, for the two processes, are converted into the more accurate γ-values, the values of the total π-electron energies are found to be:
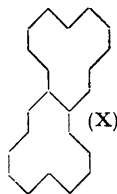
Zethrene	$24E_0 + 23.935\gamma$
(IV)	$22E_0 + 21.688\gamma$
(VII)	$22E_0 + 20.338\gamma$

Thus, (VI) is more stable than (VII) by about $1.35\gamma = 4.4$ ev. This is so large that it appears unlikely from our calculations that (VII) would be actually obtained in practice. We are more inclined to believe the suggestion of Professor M. J. S. Dewar (personal communication which we are glad to acknowledge here), that the first, easily reversible, reduction product is a monohydro-compound stabilised by resonance rather like a semi-quinone, but which, in certain circumstances, may dismutate into the dihydro-compound (VI). This interpretation cannot, however, be regarded as proved.

We have still to explain the final reduction of zethrene to the chrysene derivative (VIII). At first sight one would have expected reduction of the 5 : 11-dihydro-compound (VI) to take place by addition of hydrogen atoms at the central " olefinic " bond, giving a tetrahydro-compound. Now formation of (VIII) involves migration of the two hydrogen atoms first added. It seems probable that this migration is to positions 2 and 8. There are two reasons for this. In the first place, as Table 3 shows, the free valence at positions 2 and 8 is large, and particularly so if the activated state resembles the triplet level, where the free valence is a maximum precisely at these positions. And in the second place it can be shown from a comparison of the various calculated resonance energies that the difference in energy between the 5 : 11- and 2 : 8-dihydro-compounds is only about 3 kcal./mole. It is almost certain that the 2 : 8-compound, if it existed at all, would easily be reduced to the observed chrysene derivative (VIII). According to this picture, the reduction of zethrene proceeds first to a monohydro-compound, then to the 5 : 11-dihydro-compound; this suffers hydrogen atom migration from positions 5 : 11 to 2 : 8, either accompanied or perhaps followed by the addition of two molecules of hydrogen to give (VIII). Without the intermediate migration to positions 2 : 8, it is not easy to see how the chrysene system could be formed, nor indeed how a total of three molecules of hydrogen can be added to the parent molecule. This complete mechanism, even if it is correct, does not distinguish between the possible singlet or triplet ground states. Presumably only magnetic susceptibility measurements could do this.

In conclusion we acknowledge most warmly the kindness of Dr. Clar in telling us about this new molecule before publication of his work, and for other helpful correspondence.

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