525. *A Theoretical Treatment of the Diels–Alder Reaction. Part II. Polyenes, Arylpolyenes, and Related Molecules.*

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The reactivities towards maleic anhydride of the linear polyenes, phenylpolyenes, and various arylpolyenes are discussed in terms of the localisation theory of organic reactions, the para-localisation energies, introduced in Part I (*J.*, 1950, 691), being again used as the appropriate localisation quantities. It is shown that the theory gives an adequate interpretation of the Diels–Alder properties of these molecules when the steric factors involved are taken into account. The latter are shown to introduce some uncertainty into the making of predictions of reactivities for some molecules, and a possible method of overcoming this is mentioned.

In Part I (*J.*, 1950, 691) the reactivities towards maleic anhydride of various polycyclic aromatic hydrocarbons were discussed, and it was shown that these could be explained semiquantitatively in terms of quantities termed para-localisation energies, these being computed by the L.C.A.O. molecular orbital approximation. In the present paper polyenes, arylpolyenes, and related molecules are studied by the same method.

The application of the localisation theory to molecules of the polyene and arylpolyene type involves additional assumptions which are not required in the case of polycyclic hydrocarbons. For instance, in the latter the carbon atoms comprising the conjugated system are all coplanar, but in the case of polyenes and derivatives this is not necessarily so, rotation about carbon–carbon bonds of low mobile order being possible. In addition, with molecules of the butadiene type, carbon atoms 1 and 4 can take up two possible positions of minimum energy, only one of these, the boat configuration, being sterically favourable for a diene addition. Hence, during the following discussion it must be borne in mind that the para-localisation energies have all been computed on the assumption that the conjugated systems involved are entirely coplanar, and in discussing the relative reactivities of pairs of positions it is assumed that the latter are always orientated in the boat configuration. In those cases where either boat or chair configurations are possible and neither is favoured by other steric considerations the relative rates, k_a [as in Part I (*loc. cit.*) these represent approximations to the rates of reaction relative to anthracene ($P' = -2{\cdot}07\gamma$); more specifically $k_a = \exp. 56{\cdot}7(2{\cdot}07 - p'/\gamma)$], should be multiplied by a frequency factor expressing the probability for the molecule possessing the boat configuration, and conversely for $k_b = \exp. 56{\cdot}7(1{\cdot}77 - P'/\gamma)$ (k_b similarly represents the rate relative to that of butadiene). However, it is unlikely that the theoretical rates could give more than orders of magnitude, so this factor will be sufficiently close to unity to be neglected unless steric interactions make the boat configuration very improbable. Some such cases are discussed below.

The para-localisation energies of various pairs of positions for the linear polyenes are listed in Table I. These indicate that the reactivity decreases with increasing chain length, and also that addition to the end of the chain is preferred. Both of these generalisations are in contrast to those for the polyacenes (Part I). However, except in the case of butadiene, addition to the end of the chain (1 : 4 addition) leaves a residual molecule for which N, the number of separate conjugated systems comprising the residual molecule, is 2, whereas addition further along the chain leaves a residual molecule with $N = 3$. As pointed out in Part I, for a given value of

P or P', when N is 3 the molecule will be more reactive than when N is 2, so the question arises whether this effect is great enough to reverse the relative reactivities as indicated simply by P or P'. Addition to the polyene $C_{2n}H_{2n+2}$ leaves a residual molecule (r.m.) comprised of the polyene $C_{2n-4}H_{2n-2}$ and ethylene ($N = 2$) in the case of 1 : 4-addition. 2 : 5-Addition leaves as r.m. two radicals and ethylene, this likewise applying to addition to positions $2r : 2r + 3$ generally. Addition to any of these positions is ruled out by the relatively great instability of radicals. Addition to positions $2r + 1 : 2r + 4$ gives as r.m. the polyenes $C_{2r}H_{2r+2}$, $C_{2n-2r-4}H_{2n-2r-2}$, and ethylene, these together being less stable than the r.m. corresponding to

TABLE I.

The linear polyenes.

				P'.		
Molecule.	Position.	N.	P ($-\beta$).	($-\gamma$).	kcals.*	k_a.
Butadiene	1 : 4	1	2·47	1·77	60	2×10^7
Hexatriene	1 : 4	2	2·99	1·99	68	90
	2 : 5	3	4·99	3·59	122	—
Octatetraene	1 : 4	2	3·05	2·04	69	5
	2 : 5	3	4·69	3·32	113	—
	3 : 6	3	3·52	2·21	75	—
Decapentaene	1 : 4	2	3·07	2·06	70	2
	2 : 5	3	4·59	3·23	110	—
	3 : 6	3	3·58	2·27	77	1×10^{-5}
	4 : 7	3	4·41	3·06	104	—
Infinite polyene	1 : 4	2	3·093	2·083	71	0·5
	2 : 5	3	4·336	3·004	102	—
	3 : 6	3	3·639	2·325	79	—
	4 : 7	3	4·082	2·756	94	—
	5 : 8	3	3·714	2·392	81	—

* The conversion factor used was $\gamma = -34$ kcals. mole^{-1} as in Part I (*loc. cit.*).

TABLE II.

*Arylethylenes.**

				P'.		
Ethylene.	Position.	N.	P ($-\beta$).	($-\gamma$).	kcals.	k_a.
Phenyl	2 : 2′	1	3·44	2·42	82	10^{-9}
1 : 2-Diphenyl	2 : 2′	2	3·89	2·60	88	10^{-13}
1 : 1-Diphenyl	2 : 2′	1	3·34	2·35	80	10^{-7}
1 : 1 : 2-Triphenyl	1 : 2‴	3	4·32	2·73	93	—
	2 : 2′	2	3·84	2·54	86	—
1′-Naphthyl.....................	2 : 2′	1	3·26	2·22	75	10^{-4}
2′-Naphthyl.....................	2 : 1′	1	3·17	2·19	74	10^{-3}
	2 : 3′ [a]	1	4·2-*c*	2·8-*c*′	—	—
1′-Anthryl	2 : 2′	1	3·21	2·21	75	10^{-4}
	9′ : 10′	2	3·34	2·10	71	0·2
2′-Anthryl	2 : 1′	1	3·12	2·14	73	0·02
	9′ : 10′	2	3·32	2·08	71	0·6
	2 : 3′ [b]	1	4·2-*c*	2·9-*c*′	—	—
9′-Anthryl	2 : 1′ [c]	1	4·6-*c*	—	—	—
	9′ : 10′	3	3·79	2·26	77	2×10^{-5}
1′-Phenanthryl	2 : 2′	1	3·31 †	2·30 †	78	10^{-6}
2′-Phenanthryl	2 : 1′	1	3·23	2·25	76	10^{-5}
3′-Phenanthryl	2 : 2′ [d]	1	4·1-*c*	—	—	—
	2 : 4′	1	3·25	2·27	77	10^{-5}
4′-Phenanthryl	2 : 3′	1	3·31 †	2·29 †	78	10^{-6}
9′-Phenanthryl	2 : 10′	1	3·07	2·09	71	0·3

* *c* and *c*′ refer to conjugation energies in units of $-\beta$ and $-\gamma$, respectively. Their magnitudes are generally of the order of 0·4 and 0·2, respectively, and in the table they refer to conjugation energies for :

a, ethylene + *o*-benzoquinodimethane
b, ethylene + 2 : 3-naphthaquinodimethane
c, ethylene + 1 : 3-naphthaquinodimethane
d, ethylene + 1 : 2-naphthaquinodimethane

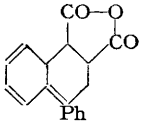
† The resonance energies of the residual molecules were computed by using the annelation energy equations (Brown, *Trans. Faraday Soc.*, in the press).

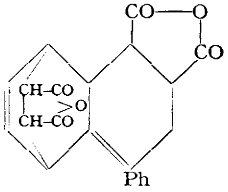
1 : 4-addition by the direct conjugation energy of the two polyenes. The para-localisation energies are computed by assuming each conjugated system in the r.m. to be quite separate in the activated complex, but the latter will always be further stabilised by indirect conjugation through the (not completely) localised carbon atoms involved in the addition. For 1 : 4-addition the neglected stabilisation of the r.m. is from the indirect conjugation energy of the two systems through the localised carbon atom 4, whereas for $2r + 1 : 2r + 4$ addition it is derived from the indirect conjugation energy of the three parts through both localised atoms. These indirect conjugation energies must necessarily be considerably smaller than the direct conjugation energy, especially as the two carbon atoms will now be approaching sp^3 hybridisation, so we may conclude that the secondary effects due to difference in the value of N for 1 : 4- and $2r + 1 : 2r + 4$-additions are not nearly sufficient to reverse the relative reactivities deduced simply from the respective values of P or P'.

These results are in excellent agreement with the scanty experimental data—hexatriene undergoes 1 : 4-addition with maleic anhydride (Kharasch and Sternfeld, *J. Amer. Chem. Soc.*, 1939, **61**, 2318; Kharasch, Nudenberg, and Sternfeld, *ibid.*, 1940, **62**, 2034), and the observation that octatetraene gives only a di-adduct (Woods and Schwartzman, *ibid.*, 1949, **71**, 1396) confirms that butadiene (the conjugated system present in the mono-adduct) is more reactive than octatetraene. It also indicates that addition to the end of the octatetraene chain is preferred.

Table II gives the para-localisation energies for various possible reactive positions (other less reactive positions being eliminated by using the principle, enunciated in Part I, that only pairs of positions giving rise to relatively stable r.m. will be reactive) for a number of arylethylenes. Considering, first, the phenylethylenes, these are known to be unreactive except 1 : 1-diphenylethylene (Bergmann and Bergmann, *ibid.*, 1937, **59**, 1443; Wagner-Jauregg, *Ber.*, 1930, **63**, 3213) for which the primary addition appears to be 2 : 2′, in good agreement with the position predicted by the data in Table II. This mono-adduct (I) contains a conjugated system equivalent to 1-phenylhexatriene fixed in a position sterically favourable for 3 : 6-addition. As seen from Table VI, these are the most reactive positions for hexatriene and considerably more reactive than the original diphenylethylene, so the second addition should occur very rapidly to give the di-adduct (II). In agreement with this, Wagner-Jauregg (*loc. cit.*; *Annalen*, 1931, **491**, 1) could only isolate the di-adduct but questioned the structure for the latter on the grounds that it behaved as saturated towards reagents such as perbenzoic acid, but it is difficult to formulate an unreactive product by any type of addition of one mole of maleic anhydride to (I).

(I.)





(II.)

The values of P' listed for the phenylethylenes are in good accord with the experimentally observed reactivities, the critical range for reactivity, in Part I fixed as between $-2{\cdot}26\gamma$ and $-2{\cdot}40\gamma$ (values for reactive 1 : 2-5 : 6-dibenzanthracene and unreactive naphthalene, respectively) being in fair agreement with the observation (Wagner-Jauregg, *loc. cit.*) that 1 : 1-diphenylethylene ($P' = -2{\cdot}35\gamma$) requires long heating to afford a satisfactory reaction. The values of P for these compounds indicate, however, that styrene ($P = -3{\cdot}44\beta$) should also be reactive (corresponding critical range for P : $-3{\cdot}51\beta$ to $-3{\cdot}68\beta$) and it does not seem possible to attribute this discrepancy to the increased amount of (neglected) indirect conjugation energy due to N having the value 1 for styrene and 2 for the compounds from which the critical range was determined. Thus it appears that P' is more reliable as a criterion of reactivity for arylpolyenes than P. The same point arises in connection with the vinylanthracenes (see below); a possible explanation for this failure will be advanced later.

The data for 1- and 2-vinylnaphthalene predict that both should add maleic anhydride, the 2-isomer being slightly more reactive. Cohen and Warren's experimental results (*J.*, 1937, 1315) confirm the reactivities; the observation of Arbuzov, Salmina, and Sharpshinskaya (*Trans. Butlerov Inst. Chem. Tech. Kazan*, 1934, No. 2, 9; *Chem. Abs.*, 1935, **29**, 3672) is presumably unreliable, the reactivity of 1-vinylnaphthalene being confirmed by Bergmann and

Bergmann (*loc. cit.*). The respective reaction conditions employed indicate that both are more reactive than 1 : 1-diphenylethylene, in good agreement with the theoretical results.

The para-localisation energy for vinylanthracenes point to 9 : 10-addition in all cases, and somewhat less readily than anthracene itself, provided the data for P' only are used. This has been confirmed by Bergmann and Bergmann (*J. Amer. Chem. Soc.*, 1940, **62**, 1699) for 2-*iso*propenylanthracene. 1- and 2-Vinylanthracene have the smallest values of P for the positions 2 : 2′ and 2 : 1′, respectively, so in these cases the values of P are so unreliable as to predict the most reactive pair of positions incorrectly. This appears to be the first definite evidence that the inclusion of the overlap integral in molecular orbital calculations of quantities such as resonance energies can improve the agreement with experiment even qualitatively.

The vinylphenanthrenes all have para-localisation energies such that addition should occur, 9-vinylphenanthrene being easily the most reactive. The latter has been found to add maleic anhydride at the expected positions (Bergmann and Bergmann, *ibid.*, 1937, **59**, 1443).

TABLE III.

Arylbutadienes.

Butadiene.	Position.	N.	P $(-\beta)$.	P'.		k_b.
				$(-\gamma)$.	kcals.	
Unsubstituted	1 : 4	1	2·47	1·77	60	1
1-Phenyl	1 : 4	2	2·94	1·96	67	2×10^{-5}
2-Phenyl	1 : 4	1	2·43	1·75	60	3
1-α-Naphthyl	1 : 4	2	2·96	1·97	67	10^{-5}
	2 : 2′	2	3·78	2·46	84	—
1-β-Naphthyl	1 : 4	2	2·94	1·96	67	2×10^{-5}
2-α-Naphthyl	1 : 4	1	2·43	1·74	59	5
2-β-Naphthyl	1 : 4	1	2·44	1·75	60	3
1-9′-Anthryl	1 : 4	2	3·00	2·00	68	10^{-6}
2-9′-Anthryl	1 : 4	1	2·43	1·74	59	5
	9′ : 10′	3	3·75	2·23	76	—

TABLE IV.

Molecule.	N.	P $(-\beta)$.	P'.		k_a.
			$(-\gamma)$.	kcals.	
1-Phenyl-1-9′-phenanthrylethylene	1	2·58	1·89	64	3×10^4
1-Phenyl-2-9′-phenanthrylethylene	2	3·11	2·12	72	0·06
1 : 2-Diphenyl-1-9′-phenanthrylethylene	2	3·48	2·23	76	10^{-4}
1 : 2-Diphenylbutadiene	2	2·91	1·94	66	2×10^3
1 : 3-Diphenylbutadiene	2	2·89	1·92	65	5×10^3
1 : 4-Diphenylbutadiene	3	3·39	2·13	72	0·03
2 : 3-Diphenylbutadiene	1	2·37	1·70	58	4×10^9
1 : 2 : 3-Triphenylbutadiene	2	2·85	1·89	64	3×10^4
1 : 2 : 4-Triphenylbutadiene	3	3·37	2·11	72	0·1
1 : 2 : 3 : 4-Tetraphenylbutadiene	3	3·33	2·08	71	0·6
1-Phenyl-4-4′-diphenylylbutadiene	3	3·40	2·13	72	0·03

The para-localisation energies of some arylbutadienes are listed in Table III. From the results it is apparent that they are all very reactive, so instead of giving the " theoretical rates " relative to anthracene, the rates relative to butadiene, k_b, have been listed. It will be noticed that addition is most favoured if the aryl portion is attached to the butadiene by the most reactive position in the former and the less reactive position in the latter. This is due to the correlation between self-polarisabilities and chemical reactivities on the one hand, and the quantitative correlation of the former with conjugation energies (Brown, *Australian J. Sci. Res.*, 1949, *A*, **2**, 566) on the other. The experimental data do not permit a comparison of relative reactivities, but it has been found that 1-phenylbutadiene adds maleic anhydride very readily (Diels, Alder, and Pries, *Ber.*, 1929, **62**, 2081), that 6-methoxy-1-vinyl-3 : 4-dihydronaphthalene, which is approximately equivalent to 2-phenylbutadiene, is reactive even at room temperature (Dane, Höss, Bindseil, and Schmitt, *Annalen*, 1937, **532**, 39), and that 1-α-naphthyl-1 : 3-butadiene undergoes 1 : 4- rather than 2 : 2′-addition (Arnold and Coyner, *J. Amer. Chem. Soc.*, 1944, **66**, 1542).

When several aryl groups are attached to the one polyene, the possibility arises of steric interactions preventing the molecule assuming a configuration favourable for addition. Some such molecules are considered in Table IV. The first three compounds listed would be expected to be reactive, although probably less so than anthracene, as judged solely by the respective para-localisation energies, the reactive positions being the ethylene carbon and the 10′-phenanthrene carbon atom in each case. Scale drawings of these reveal that the first and the third would exist preferably in the chair form (for the reactive four-carbon system) when planar, 1-phenyl-2-9′-phenanthrylethylene being the only one for which the planar boat configuration does not involve excessive hydrogen interactions. This is in agreement with the observation (Bergmann and Bergmann, *locc. cit.*) that, of the three, only the last compound added maleic anhydride. A similar interpretation seems reasonable for Craig's work on *cis*- and *trans*-piperylene (*J. Amer. Chem. Soc.*, 1943, **65**, 1006; cf. Norton, *Chem. Rev.*, 1942, **31**, footnote, p. 349), rendering questionable its support of a two-stage addition mechanism for the Diels–Alder reaction (Dewar, " Electronic Theory of Organic Chemistry," p. 151).

TABLE V.

*The αω-diphenylpolyenes.**

			P'.		
Diphenylpolyene.	Position.	$P\ (-\beta)$.	$(-\gamma)$.	kcals.	k_a.
Butadiene	1 : 4	3·39	2·13	72	0·03
Hexatriene	1 : 4	3·48	2·20	75	5×10^{-4}
Octatetraene	1 : 4	3·47	2·20	75	5×10^{-4}
	3 : 6	3·56	2·27	77	1×10^{-5}
Decapentaene	1 : 4	3·44	2·18	74	0·002
	3 : 6	3·55	2·26	77	2×10^{-5}
Dodecahexaene	1 : 4	3·41	2·16	73	0·005
	3 : 6	3·53	2·25	76	3×10^{-5}
	5 : 8	3·54	2·26	77	2×10^{-5}

* For all additions considered in this table, *N* is 3.

TABLE VI.

The 1-*phenylpolyenes.*

				P'		
Polyene.	*N*.	Position.	$P\ (-\beta)$.	$(-\gamma)$.	kcals.	k_a.
Ethylene	1	2 : 2′	3·44	2·42	82	10^{-9}
Butadiene	2	1 : 4	2·94	1·96	67	500
Hexatriene	3	1 : 4	3·47	2·18	74	0·02
	2	3 : 6	3·05	2·04	69	5
Octatetraene	3	1 : 4	3·54	2·24	76	5×10^{-5}
	3	3 : 6	3·59	2·27	77	10^{-5}
	2	5 : 8	3·07	2·06	70	2

Of the four diphenylbutadienes, the 1 : 3- and the 1 : 4-isomer can assume the requisite planar boat structure, so it is to be expected that these will add maleic anhydride, the former more readily than anthracene, the latter perhaps less readily [for this *N* is 3, so a direct comparison of *P*′ with that of anthracene, for which *N* is 2, is not permissible (see Part I, also discussion above)]. Kuhn and Wagner-Jauregg (*Ber.*, 1930, **63**, 2662) found that 1 : 4-diphenylbutadiene gave a mixture of isomeric adducts; 1 : 3-diphenylbutadiene does not seem to have been studied. The 1 : 2- and 2 : 3-diphenylbutadienes are probably not coplanar either for boat or for chair configurations of the butadiene system. However, this presumably is not sufficient to inhibit the (otherwise very ready) addition, because Bergmann and Bergmann found that 1 : 2-diphenyl-4-methylbutadiene was reactive, and 2 : 3-diphenylbutadiene has been found to react even in benzene (Allen, Eliot, and Bell, *Canadian J. Res.*, 1939, **17***B*, 75).

The sequence 1 : 2 : 4-triphenyl-, 1 : 2 : 3-triphenyl-, 1 : 2 : 3 : 4-tetraphenyl-butadiene represents increasing steric opposition to the assumption of a planar boat configuration. The fact that the first does and the last does not add maleic anhydride (Bergmann and Bergmann, *J. Amer. Chem. Soc.*, 1940, **62**, 1699; Bergmann, Winter, and Schreiber, *Annalen*, 1933, **500**, 122) in spite of the opposite tendencies as evinced by the para-localisation energies demonstrates again the importance of these steric considerations. It seems likely, in view of its very low para-localisation energy, that 1 : 2 : 3-triphenylbutadiene will add maleic anhydride fairly readily, but the uncertainty about steric conditions precludes any more definite prediction.

The last compound in Table IV should from the theoretical results be very similar in reactivity to 1 : 4-diphenylbutadiene. It has been shown to react with maleic anhydride in excellent yield (Bergmann and Weizman, *J. Org. Chem.*, 1944, **9**, 415).

The diphenylpolyenes (Table V) present some interesting results. Of the lower members of the series, diphenylbutadiene is the most reactive and diphenylhexatriene the least; the reactivity then slowly increases, tending to that of diphenylbutadiene. Addition of one mole of maleic anhydride to diphenyloctatetraene yields an adduct containing a conjugated system equivalent to that of 1-phenylbutadiene. The latter adds another mole of maleic anhydride to give the di-adduct more rapidly than the original molecule, as judged from the respective values of P', so it should only be possible to detect the di-adduct, even with a deficit of anhydride, as observed by Kuhn and Wagner-Jauregg (*loc. cit.*). Diphenyldecapentaene again is most reactive at the 1 : 4-positions, the mono-adduct containing the 1-phenylhexatriene system. As seen from Table VI, this is most reactive at the 3 : 6-positions and again only the di-adduct would result. Kuhn and Wagner-Jauregg claimed to prove that the di-adduct is formed by 1 : 4- and 7 : 10-additions (corresponding to 1 : 4-addition in the phenylhexatriene portion) by converting it into di-4′-diphenylylethylene; however, they describe two different di-adducts and it is not clear whether the proof applies to both or not. Also in molecules such as diphenyldecapentaene reactivity of certain positions is dependent upon favourable steric conditions which may not be attainable.

Conclusion.—The theoretical results just considered again afford a satisfactory interpretation of the available experimental results. In some cases the theoretical predictions are less certain owing to lack of knowledge of the precise stereochemistry of the molecule in question. For some molecules, where the question is mainly that of approximate coplanarity or not, the latter could perhaps be decided by spectrographic studies; however, it would first be necessary to establish whether coplanarity of the 4-carbon system involved in the reaction is required for addition. When the chair structure is more stable, the activation energy for chair–boat conversion will be one of the factors determining whether addition will occur at a reasonable rate. In cases where the alternative boat structure involves steric interactions, there seems little hope of discussing the Diels–Alder properties by the present simple theory, but when these are absent it may prove possible to extend the present theory by use of quantities B_s and B_s' (the energies required to convert a given bond of a conjugated system into a pure single bond) which are calculable in a manner very similar to that used for P and P'.

In the above discussion of theoretical data it emerged that P' was more reliable than P when considering the Diels–Alder properties of arylpolyenes. This may possibly be connected with the fact that the resonance energies of polyenes, computed with $S = 0$, seem to be too great. For example, the values of β and γ deduced from Dewar's data (*loc. cit.*) for benzene, naphthalene, and anthracene are $-17._1$ and $-33._6$ kcals., respectively. These parameters lead to the following resonance energies (kcals.) :

	From R.	From R′.		From R.	From R′.
Butadiene	8	6	Hexatriene	17	13

whereas data from heats of hydrogenation (Wheland, " The Theory of Resonance," p. 56), although not completely reliable (cf. discussion by Dewar, *loc. cit.*), indicate values around 4 kcals. for butadiene. Thus there is probably a variable over-estimation of the stability of polyenes, and possibly also in smaller degree for arylpolyenes, when using R, and this will result in P being too small an estimate of the para-localisation energy when the r.m. contains polyene systems in place of cyclic systems in the original molecule. Hence P will indicate too great a reactivity for molecules such as styrene, for which the r.m. is hexatriene for the most reactive pair of positions.

Similar considerations do not apply to the polycylic hydrocarbons considered in Part I because for these the r.m. are also cyclic systems. For the polyenes, both original and residual molecules contain polyene systems, so this effect may cancel out to some extent. The underlying cause of the discrepancies for polyenes and arylpolyenes is doubtless the unsystematic variation of σ-bond energies accompanying addition as opposed to the systematic variation for polycylic hydrocarbons.

In subsequent papers phenyl derivatives of aromatic systems, together with extensive theoretical data for polycyclic systems for subsequent experimental testing, will be considered.

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