NOTES

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Photocyclization of *o*-Terphenyl-Type Compounds and Reactivity Indices[1]

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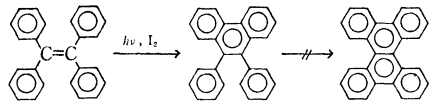
The photocyclodehydrogenation of stilbene and *o*-terphenyl type compounds has been throughly explored and is utilized as a synthetic means for a number of polycondensed aromatic and heteroaromatic compounds.[1,2]

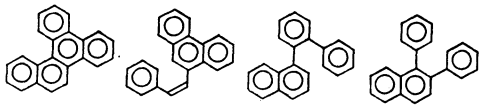


I II

For certain type of compounds, however, the photocyclization reaction did not take place: Mallory and co-workers[3] reported the failure to obtain dibenzo[*g,p*]chrysene (II) by the attempted photolysis reaction of 9,10-diphenylphenanthrene (I), although the formation of the latter was easily achieved by the irradiation of tetraphenylethylene in the presence of iodine. They attributed the inertness of I toward further cyclization reaction to a low electron density on the carbon atoms undergoing coupling. The failure of cyclization with 1,2,3-triphenylazulene,[4] 1,2,3,4- and 1,2,4,5-tetraphenylbenzenes[5] and 1,2,3-triphenylnaphthalene[5] was explained by steric reasons. 1,1'-Binaphthyl was also found to resist toward cyclization.[6] We have reported the failure of the attempted photocyclization of diphenylquaterphenyl (XVII),[1] although 2,2'-diphenylbiphenyl (XII) was smoothly converted to dibenzo[*fg, op*]naphthacene.[1,7]

For compounds where different way of cyclization is possible, some give more than one product but others result in a selective cyclization. The cyclization of 1,2-dipyridylethylene[8] or styrylpyridines[9] was shown to be possible in a dual way or more, whereas 1,2-di-β-naphthylethylene[10] gave only benzo[*g,h,i*]perylene, indicating that two other possible cyclization modes are unimportant.

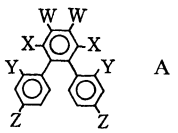
When several routes are conceivable for the construction of a certain ring system the selection of the method is left to one's choice or is determined by the availability of the starting materials. For example, benzo[*g*]chrysene (III) will be produced from either IV,[11] V,[12] or VI (not tested).



III IV V VI

In order to give a measure for the occurrence or otherwise of the cyclization reaction, to predict the product where several routes are conceivable, and to select the most efficient way to a given ring system, one can rely on the calculation of the reaction indices.

We have carried out the calculation of free valence numbers and localization energies for a series of *o*-terphenyl type compounds by the simple HMO method, expecting these figures be served as a criterion for the occurrence of the photocyclization reaction. Model compounds we studied are shown by a general formula A, where phenyl group(s) is introduced at W—Z positions. The *o*-terphenyl–triphenylene reaction is selected, since it is regarded as the basic reaction for the synthesis of polycondensed aromatics.[1,7,13,14]



A

From these models we may learn both the electronic and steric effects of the phenyl substitution on the cyclization of *o*-terphenyl compounds. Phenyl group(s) at X or Y position is capable of entering into further cyclization reactions.

The sum of free valence numbers in the first excited state, $\sum Fr^*$, was calculated for the atoms undergoing photo-coupling, location of which being shown by a dotted line. These figures together with localization energies, L^*, are summarized in Table 1. Compounds

1) Photo-Aryl Coupling and Related Reactions. VIII. Part VII: T. Sato, S. Shimada, and K. Hata, This Bulletin, **44**, 2484 (1971).

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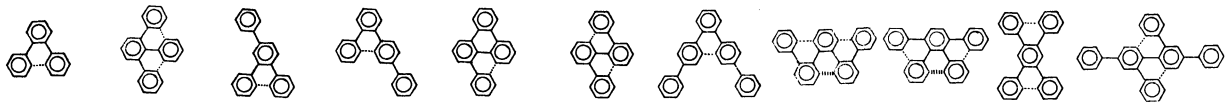
TABLE 1. FREE VALENCE NUMBERS IN THE FIRST EXCITED STATE, $\sum Fr^*$, AND LOCALIZATION ENERGIES, L^*, FOR A[a)]



	VII[1,13)]	VIII[1,7)]	IX[1)]	X[14)]	XI[1,7)]	XII[1,7)]	XIII[14)]	XIV	XV[5)]	XVI[5)]	XVII[1)]
$\sum Fr^*$	1.027	1.003	0.981	0.967	0.962	0.949	0.949	--- 0.918 IIIII 0.926	IIIII 0.909 --- 0.955	0.955	0.925
L^*	3.320	3.349	3.427	3.458	3.369	3.423	3.537	--- 3.484 IIIII 3.485	IIIII 3.426 --- 3.421	3.601	3.589

a) Free valence numbers shown in the Table are the sum of the values obtained for the atoms undergoing coupling, the location of which being shown by --- or IIIII

I through XIII, listed in the order of decreasing $\sum Fr^*$, were successfully converted to the corresponding polycondensed aromatic compounds by the photolysis reactions using iodine as an oxidant.[1,7,13,14)]

Compounds XV and XVI were reported to be inert under the conditions studied.[5)] The reaction of XIV is not examined yet.

Critical values deduced from Table 1 are $\sum Fr^* > 0.95$ and $L^* < 3.54$, for which the cyclization is possible. Recently Laarhoven and co-workers[5)] proposed that the reaction is possible if $\sum Fr^* > 1$ and $L^* < 3.45$. They considered the photocyclization of tetraphenylethylene, $\sum Fr^* = 0.965$, to be exceptional, although from our results the conversion to I could be predictable. The Table by Laarhoven[5)] listing non-photocyclizing cases appear to contain those compounds of which inertness is explainable not by the free valence consideration but from two other reasons; 1) non-existence of the intermediate dihydro structures, and 2) steric inhibition by neighboring bulky groups.

The failure due to the first case include the lack of cyclization in α,α′-dinaphthyl,[6)] and a related compound.[5)] Assumably a steric factor becomes important when more than four benzene rings occupy vicinal position as in XV[5)] since 1,2,3-triphenylbenzene VIII is photocyclizable.[1,7)] A fused ring with a phenyl substitution is considered to cause a similar steric inhibition. This explains the inertness of II, 1,2,3-triphenylnaphthalene,[5)] 1,2,3-triphenylazulene *etc.*[4)]

In the cases of VIII and XII, a double cyclization reaction occurred and yet we could not trap intermediate XI. This is understood since XI is also a photocyclizable molecule.

The failure of XVI to undergo photocyclization, however, can not be explained and should be treated as exceptional.

More refined treatments considering the non-planarity of the molecule will make the situation clearer.

As far as the simple molecular orbital calculations concern, further accurate discussions could not be done. Some investigaters[15–17)] have made calculations to see if a relation exists for excited states between static and dynamic reactivity indices. However, they have not found out any correlation at all and the situation is the same in the present work as is seen in Fig. 1.

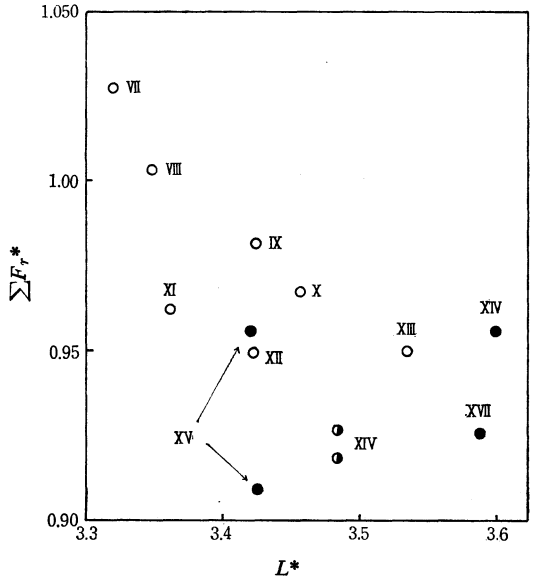


Fig. 1. The relation between $\sum Fr^*$ and L^* for those compounds that underwent photocyclization (○) and that did not (●). Compound XIV (◑) has not been examined.

The failure in obtaining a relationship between static and dynamic reactivity indices would be presumably due to the following factors: 1) Firstly, excited state molecular orbitals used in estimating reactivity indices are those obtained from minimization of ground state energy and not of excited state energy. 2) Secondly, localization energies are usually expressed in terms of π-electron energies. In discussing reactivity of molecules, localization energies should be expressed in terms of bond energies as pointed out by Dewar *et al.*[18,19)] Some improvements might be expected, if we do this.

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