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Note

Reactivity of Maleic Anhydride with Polycyclic Hydrocarbons with *Open* Ends

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It is well known that 1 : 14-benzbisanthrene readily adds maleic anhydride, forming an adduct which yields ovalene on decarboxylation and dehydrogenation. The corresponding conversion of 1 : 12-benzperylene into coronene proceeds only under the most forcing conditons. Trotter who carried out the structural investigations[1,2] on both 1 : 14-benzbisanthrene and 1 : 12-benzperylene put forward an explanation for such behaviour based on the assumption of greater bond fixation in 1 : 14-benzbisanthrene than in 1 : 12-benzperylene.

We would like to reformulate this explanation by use of the free valence concept[3]. Free valence can be regarded as the molecular orbital equivalent of Thiele's residual affinity and it correlates roughly with reactivity of an atom in the molecule for certain reactions and it is valid for alternant polycyclic hydrocarbons[4–6]. Therefore, we point out that the reaction of adding maleic anhydride to a polycyclic hydrocarbon with *open* end is governed by the degree of the unsaturation of the relevant carbon atoms. We have calculated free valence indices from Hückel molecular orbitals for the two carbon atoms at the *open* ends of 1 : 14-benzbisanthrene and 1 : 12-benzperylene.

Calculations were carried out on a CEA 90—40 computer. For $N_{max}\sqrt{2}$ is used as recommended by Burkitt, Coulson, and Longuet-Higgins[7] for secondary carbon atoms. The following free valence indices are obtained for relevant carbon atoms: 0.1472 (1 : 14-benzbisanthrene) and 0.1388 (1 : 12-benzperylene). It is quite clear that 1 : 14-benzbisanthrene having greater values of free valence at the *open* end will add maleic anhydride a great deal easier than 1 : 12-benzperylene. This is in agreement with observed behaviour. To conclude, we mention that the same explanation is valid, also, for the difference in behaviour between perylene and bisanthrene when maleic anhydride is added to them.

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IZVOD

Reaktivnost anhidrida maleinske kiseline prema policikličkim ugljikovodicima s *otvorenim* krajevima

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Reaktivnost ugljikovih atoma na *otvorenim* krajevima 1:14-benzbisantrena i 1:12-benzperilena prema anhidridu maleinske kiseline objašnjena je primjenom koncepcije slobodne valencije. Prema tome 1:14-benzbisantren koji ima više vrijednosti slobodne valencije na *otvorenom* kraju adirat će anhidrid maleinske kiseline znatno lakše nego 1 : 12-benzperilen. To se slaže s opaženim ponašanjem. Isto objašnjenje vrijedi i za različito ponašanje perilena i bisantrena pri adiranju anhidrida maleinske kiseline.

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ZAGREB

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