Nuclear Magnetic Resonance Evidence for Stereospecific Ground-state Interactions between Ethylenes and Benzene

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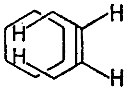
Summary N.m.r. evidence indicates a preferred *exo*-orientation in liquid mixtures of ethylenes and benzene when the ethylene is an acceptor relative to the benzene, and an *endo*-orientation when the ethylene is a donor: these orientations match the stereospecificities observed in the corresponding 1,2-photoaddition reactions.

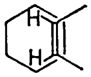
The stereospecific *endo*- and *exo*-1,2-photoadditions of ethylenes to the benzene ring[1,2] have prompted a search for possible ground-state interactions utilising the known relationships between orientation and magnetic screening.[3]

The systems examined have included benzene (I.P. 9·2 eV) with the acceptors maleimide, methyl vinyl ketone, and acrylonitrile, (I.P. $>$ 9·6 eV), and the donors *cis*- and *trans*-but-2-ene, *cis*-di-t-butylethylene, cyclopentene, cyclohexene, cycloheptene, *cis*- and *trans*-cyclo-octene, norbornene, ethyl vinyl ether, and *cis*- and *trans*-dimethoxyethylene (I.P. $\leqslant$ 9·13 eV). Benzene and alkylbenzenes were studied with maleic anhydride as the acceptor.

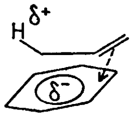
The n.m.r. spectra (60 MHz) of the ethylenes were measured at 35° using 1·5 mol. % solutions in the aromatic component and, for reference, solutions in CCl_4.[4] All measurements were made in duplicate and some in triplicate, with excellent reproducibility.



(I)



(II)



(III)

With all the donor ethylenes, benzene induced small (*ca.* 5 Hz) downfield shifts of the vinyl protons and comparable upfield shifts of allylic or alkoxy protons. In the case of *cis*-di-t-butylethylene, benzene induced an 8 Hz downfield shift of the vinyl protons, but the resonance due to the methyl protons was unchanged (<1 Hz), possibly as a result of time-averaging between the 9 t-butyl protons.

In contrast, all the acceptor ethylenes exhibited marked upfield shifts of the vinyl protons (*ca.* 30—90 Hz).

These findings imply a preferred *endo*-orientation between benzene and the donor ethylenes [diagram (I)], and an even more strongly preferred *exo* orientation between benzene and the acceptor ethylenes [diagram (II)]. It is interesting, and possibly relevant, that these preferred ground-state orientations precisely match the stereospecificities observed in the corresponding 1,2-photoaddition reactions, although the tendency for 1,2-photoadditions to occur depends on steric factors and the magnitude of ionisation potential differences between the addends.[1]

In mixtures of benzene with acceptor ethylenes, the magnitude of the benzene-induced upfield shifts increases with increasing ionisation potential of the ethylene, but where the ethylene is a donor [as for example with *cis*-cyclo-octene and benzene (−4 Hz), toluene (−3 Hz), and benzonitrile (−2 Hz), or with benzene and *cis*-but-2-ene (4 Hz, I.P. 9·13 eV) and *cis*-dimethoxyethylene (−5 Hz, I.P. 7·97 eV)], no clear relationship between the magnitudes of the downfield chemical shifts of vinyl protons and ionisation potential differences is apparent.

With maleic anhydride and alkylbenzene donors, the magnitude of the aromatic-induced upfield shifts appears to depend on steric and polar factors, as may be seen from the values 93, 89, 86, 80, 80, 95, 86, and 90 Hz found for the series PhH, PhMe, PhEt, $PhPr^i$, $PhBu^t$, o-$C_6H_4Me_2$, p-$C_6H_4Me_2$, and 1,3,5-$C_6H_3Me_3$ respectively: *cf.* ref. 5.

The slight tendency for *endo* association between benzene and donor ethylenes does not give rise to charge-transfer absorption, and is particularly surprising. It may arise from weak π-bonding involving the allylic or alkoxy hydrogen atoms since these should have enhanced δ+ character as a result of any net transfer of charge from the ethylene to the aromatic ring: see diagram (III).

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