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SOME π-MOLECULAR COMPLEXES SHOWING NO CHARGE TRANSFER SPECTRA FORMED BY P-TOLUENESULFONIC ESTERS.[1]

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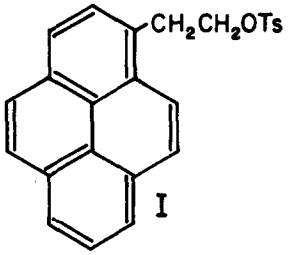
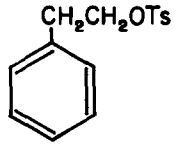
It is well recognized that aromatic hydrocarbons form weak complexes with suitable acceptors, both intramolecularly[3] and intermolecularly[4], the formation of such complexes being signalled by the appearance of new bands in the uv-visible spectrum due to charge transfer transitions. In view of this behavior, and a theoretical interpretation by Mulliken[5], complexes of this kind are now commonly referred to as "charge transfer complexes" or "donor-acceptor complexes" and most chemists are clearly under the impression that they represent a special type of molecular association in which the components are held together primarily by "charge transfer forces."

In a recent communication[6] it was pointed out that this argument is fallacious, and that π-molecular complexes of this kind are best regarded as normal van der Waals aggregates. The fact that most known examples show obvious charge transfer bands in their spectra is due to artificial selection; for nearly all the work in this area has made use of spectroscopic techniques. It was pointed out[6] that many analogous complexes should exist in which the charge transfer bands are obscured by those due to locally excited transitions and whose existence could not therefore be detected by spectroscopic studies. We wish to report some examples of this kind, involving both intra- and intermolecular complexing, in which p-toluenesulfonate esters act as "acceptors."

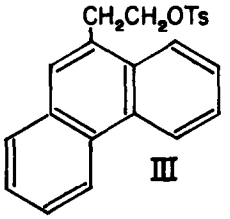
In the proton nmr spectra (Table I) of 2-(1-pyrenyl)ethyl p-toluenesulfonate (I), the signals due to the protons in the tosyl group show remarkably large upfield shifts in comparison with those in alkyl tosylates or 2-phenylethyl tosylate (II). This effect cannot be due simply to the bulk of the aryl groups in I since the resonances for the tosyl protons show a surprisingly large dependence on temperature, the difference from those in II increasing as the temperature is decreased. (Note that the signal for the α-methylene group remains unchanged.) Furthermore, addition of ca. one mole of 2,3-dichloro-5,6-dicyanoquinone (DDQ) to I dissolved in chloroform-d gave a deep purple solution in which the nmr signal due to the tosyl methyl protons showed a large downfield shift (16 Hz) relative to I. No such shift was observed when DDQ was added to a solution of II in chloroform-d, although here again an intense color developed.



I



II



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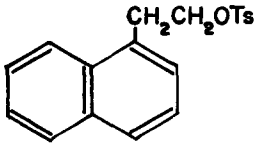

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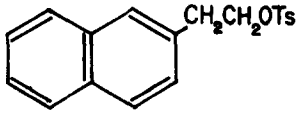
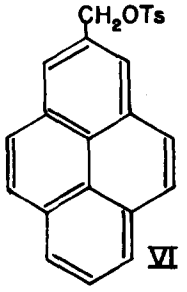


V



VI

TABLE I

NMR Spectra of $RCH_2^AOSO_2$

Compound	Temperature	Solvent	Chemical shift[a] in Hz relative to tetramethylsilane for proton: A[b]	B[c]	C[c]	D
I	room	$CDCl_3$	262	439	396	105
	room	$CHCl_2CHCl_2$	265	442	403	112
	0	$CHCl_2CHCl_2$	262	435	395	102
	-48	$CHCl_2CHCl_2$	264	424	381	84
I+DDQ(1:1)	40	$CDCl_3$	267	445	409	118
II	room	$CDCl_3$	254	463	437	145
II+Pyrene(1:1)	room	$CDCl_3$		d	d	140
III	40	$CHCl_2CHCl_2$	263	d	417	133
	-48	$CHCl_2CHCl_2$	264	d	409	134
IV	room	$CDCl_3$	261	d	d	141
V	room	$CDCl_3$	258	d	d	138
VI	room	$CDCl_3$		469	433	138

(a) Spectra were measured using 6% (w/w) solutions and a Varian A60 spectrometer.

(b) Center of triplet.

(c) Center of doublet.

(d) Resonances obscured by aromatic multiplet.

The only reasonable explanation of these results seems to lie in internal π-molecular complex formation between the pyrenyl and tosyl groups in I. Examination of Courtauld models shows that both rings can lie parallel to one another at their van der Waals distance, without any angle strain in the intervening chains. In this conformation, the protons of the tosyl group lie

over the face of the pyrenyl in a region where they will be subject to strong diamagnetic shielding by ring currents in the pyrenyl rings. DDQ is known[7] to form unusually strong complexes with aromatic hydrocarbons; the shift in the methyl resonances of I on adding DDQ can then be attributed to preferential complexing between it and pyrenyl, freeing the tosyl group from the shielding association with the pyrenyl moiety. The shift in the methyl signal cannot of course be due simply to complex formation with DDQ; for no shift was observed on addition of DDQ to II. These differences between I and II can also be explained in terms of internal complex formation; for benzene forms much less stable complexes than does pyrene or phenanthrene[4,6]. The effect of an increase in temperature on the nmr spectrum of I is also easily explained on this basis; for an increase in temperature should decrease the proportion of I that is internally complexed.

Naphthalene and phenanthrene form complexes that are intermediate in stability between benzene and pyrene; the proton nmr spectrum of 2-(9-phenanthyl)ethyl tosylate (III) again indicates shielding of the ring protons of the tosyl group. This effect is, as expected, less than in I, but it likewise increases with decreasing temperatures. No shift is observed in the case of the methyl protons of III; however examination of Courtauld models of III in the internally complexed form indicates that the methyl group should lie above the edge of the phenanthrene ring system, in a region which would probably be neither shielded nor deshielded. The same applies to the corresponding α-(IV) and β-naphthylethyl tosylates; here the protons of the tosyl group could not be resolved from those of naphthyl.

Examination of Courtauld models shows that in arylmethyl tosylates the aromatic rings can no longer lie opposite and parallel without introducing much strain into the intervening chain. The fact that the tosyl protons in 2-pyrenylmethyl tosylate (VI) absorb at almost exactly the same frequencies as those in II (Table I) therefore provides further confirmation of our interpretation.

As a final check, we tried adding pyrene to a solution of II in chloroform-d. The methyl protons of II showed a significant upfield shift, as would be expected if tosyl esters can in fact form stable complexes with pyrene. The extent of complexing was admittedly much less than in I; this, however, would be expected, since intermolecular associations are always formed less easily than corresponding intramolecular ones, due to the loss of translational entropy in the former case.

The esters used in this study were made for another purpose and their preparation will be described elsewhere. All gave satisfactory analyses, etc.

REFERENCES

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(2) N.A.S.A. Trainee.

(3) See e.g. W.N. White, J.Am.Chem.Soc. 81, 2912 (1959); D.J. Cram and M. Cordon, ibid. 77, 4090 (1955).

(4) See L.J. Andrews and R.M. Keefer, Molecular Complexes in Organic Chemistry, Holden-Day Inc., San Francisco (1964).

(5) R.S. Mulliken, J.Am.Chem.Soc. 74, 811 (1952); J.Phys.Chem. 56, 801 (1952); J.Chim.Phys. 61, 20 (1964).

(6) M.J.S. Dewar and C.C. Thompson Jr., Tetrahedron Suppl. 7, 97 (1966).

(7) See D. Walker and J.D. Hiebert, Chem.Rev. 67, 153 (1967).