Tetrahedron Letters No.15, pp. 1337-1341, 1967. Pergamon Press Ltd. Printed in Great Britain.

DICARBONIUM IONS IN THE BIPHENYL SERIES

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(Received 3 January 1967)

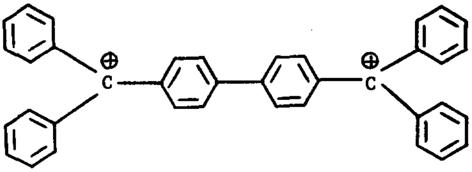
Some time ago (1) we reported on dicarbonium ions of the triarylmethyl type in which the sites of ionization were attached ortho, meta or para on a single benzene ring. We now wish to record results (2) on the spectra and $pK_{R^{++}}$'s of dicarbonium ions in which the ionization sites are separated by two benzene rings, particularly since our approach differs from and complements one which was recently reported in this journal (3).

Carbinols corresponding to dications I-IV were synthesized, and their spectra determined as a function of acid strength in aqueous sulfuric acid. The spectra and $pK_{R^{++}}$'s of the dications are given in Table I (4).

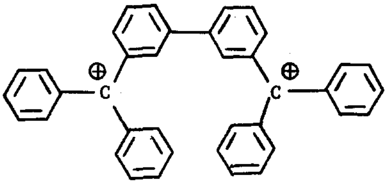
Once can view ions I-III as having been derived by joining two trityl cations (Tr^+) respectively at the para, meta or ortho positions. If one ignores the question of coplanarity of the biphenyl system, resonance structures can be drawn for I and III in which both positive charges can be distributed in any of the six rings, whereas the two trityl cations in II are, to a first approximation, isolated. Expected twisting should also isolate the charges in III.

In molecular orbital terms, one anticipates that the joining of two trityl cations at the para or meta positions would result in patterns of m.o.'s shown in FIG. I, because the NBMO of Tr^+ has sizable coefficients in the para positions, but zero coefficients in the meta positions. Provided that the splitting of the two highest filled orbitals (HBMO) were the same in the two cases, one would predict that the para dications (I) should absorb at longer wavelength than the meta dication (II).

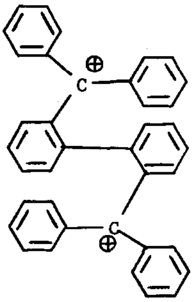
The observed spectra are in accord with these qualitative predictions (see Table I). II and III have spectra similar to Tr^+, whereas I absorbs at considerably longer wavelength. IV, in which the biphenyl system is constrained to a planar arrangement, absorbs at even longer wavelength than I, where some twisting (~20°) may be expected (5).



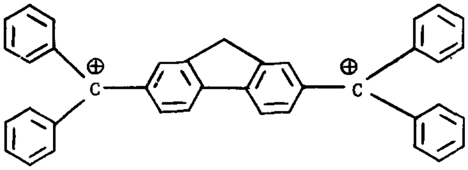
I



II



III



IV

Because it reportedly gives energy values and charge densities for organic cations which are improved over the simple Huckel method, the ω-technique (6,7) has been applied to these dications. FIG. II gives a plot of Δm (the energy difference between the highest occupied and lowest unoccupied m.o.'s) *vs* the position of longest absorption maximum for several carbonium ions (8). The line is arbitrarily drawn through the points for the trityl and fluorenyl cations. The fit is quite good except for II which has a calculated Δm nearly identical with that of I, despite the qualitative expectations from FIG. I. Detailed examination of the m.o. calculations shows that the root of the discrepancy lies in appreciably larger splitting of the HBMO's in II than in I (the NBMO's behave as shown in FIG. I). We are forced to conclude that either the ω-technique gives an unrealistic picture

TABLE I

Spectra and $pK_{R^{++}}$ of Dicarbonium Ions in Sulfuric Acid

Ion	λ_{max} (ε)	$pK_{R^{++}}$
I	530 (90,000) 442 (53,500) 410 (34,500)	- 8.2
II	430 (67,500)	- 8.4
III	428 (35,500) 390 (24,000)	-15.0
IV	568 (152,000) 525 (46,000) 440 (35,000)	
Tr^+	432 (37,500) 408 (36,500)	- 7.4

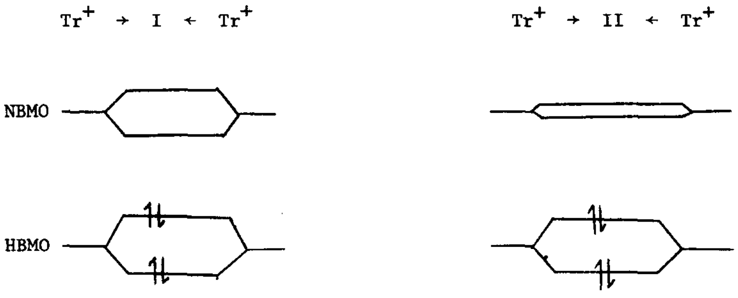


FIG. I.
Predicted Result of Joining Two Triphenylmethyl Cations (Tr^+) at the Para or Meta Positions

for II, but is satisfactory for all the other ions in FIG. II, or more likely, that the central single bond in II is twisted much more than the 20° used in the calculation.

The $pK_{R^{++}}$'s require some comment. The difference between the first and second ionizations leading to I and II are too small to be observed. The very low $pK_{R^{++}}$ of III is due to the fact that the monocation is the cyclic oxonium ion V, a cation which is more stable than the monocations derived from I and II and which must be doubly protonated to produce III. The ether corresponding to V is obtained when solutions of III are hydrolyzed.

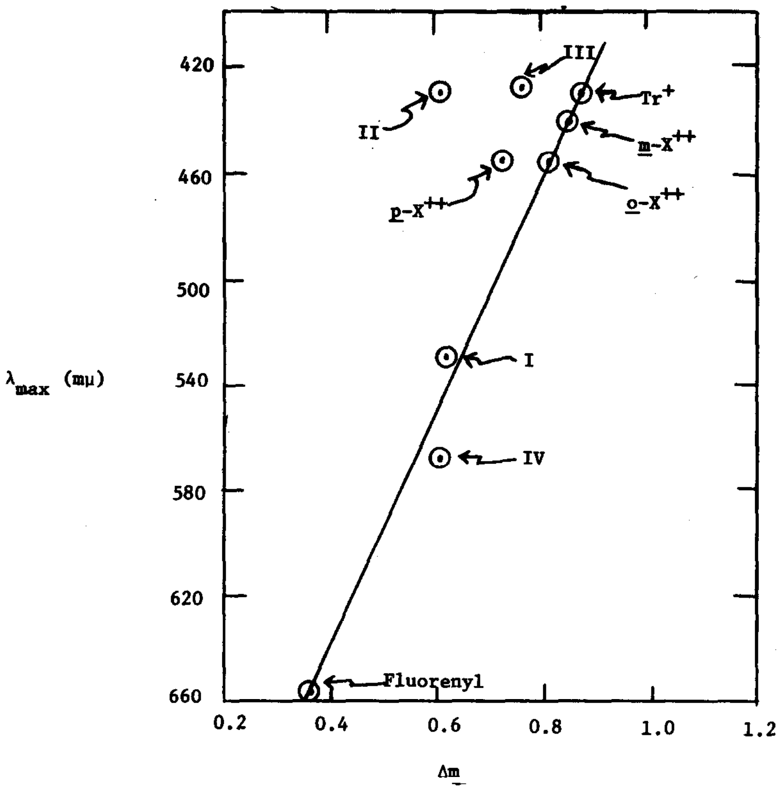
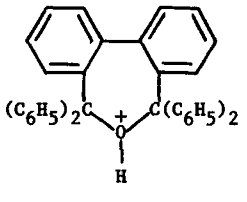


FIG. II. Correlation of Absorption Maxima with Δm-values Calculated by the ω-Technique. (Symbols are defined in the text except for X^{++}, which represents the tetraphenylxylyl dications; see ref. 1)



Acknowledgement: We are grateful to the National Science Foundation for support of this work.

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2. Taken in part from the Ph.D. Thesis of T. Sulzberg, Michigan State University, 1962.
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4. The spectrum of I agrees well with that reported by W. Theilacker and W. Ozegowski, Ber., 73, 898 (1940); that of Tr^+ agrees with that reported by N. C. Deno, J. J. Jaruzelski and A. Schriesheim, J. Am. Chem. Soc., 77, 3044 (1955). The reported pK is -6.7; we used a slightly different acidity scale, due to E. M. Arnett and R. D. Buchick, ibid., 86, 1564 (1964).
5. H. Suzuki, Bull. Chem. Soc. Japan, 32, 1340 (1959).
6. A. Streitwieser, Jr., Molecular Orbital Theory for Organic Chemists, John Wiley and Sons, New York, 1961, p. 115.
7. Assumptions were $\omega = 1.4$, $\beta = \beta_0 \cos \theta$ for non-planar conformations. 'Outer' rings were assumed to be twisted 30° [compare 23°, D. E. Reilly and H. P. Leftin, J. Phys. Chem., 64, 1555 (1960); 35°, A. H. Gomes de Mesquita, C. H. MacGillavry and K. Eriks, Acta Cryst., 18, 437 (1965) and 45°, N. C. Deno, P. T. Graves and G. Saines, J. Am. Chem. Soc., 81, 5790 (1959)] and biphenyl rings twisted 20° (see ref. 5) except for the fluorenyl ions, where 0° was used, for III, where 70° was used [H. Suzuki, Bull. Chem. Soc. Japan, 32, 1350 (1959)], and for $o\text{-}X^{++}$ where 90° was used at the 'central' ring. Δm values were limited to interacting orbitals; i.e., orbitals isolated in the outer rings were not used to determine Δm's.
8. A similar plot, using HMO transitions energies assuming flat carbonium ions is given in ref. 6, p. 229. This graph unfortunately includes several incorrect λ_{max} (9) which, if corrected, improve the correlation.
9. H. Hart and T. Sulzberg, J. Org. Chem., 28, 1159 (1963).