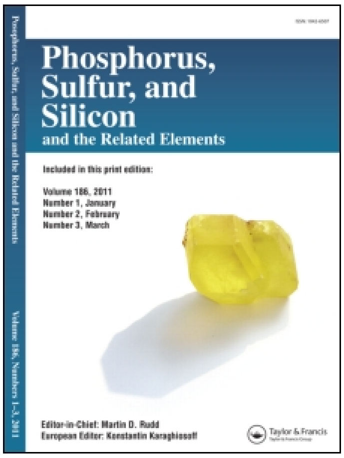


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Novel Colored Systems of the "Inverted Triphenylmethylium Dye" Type Containing Nitrogen, Phosphorus, Sulfur and Congeneric Donor Centers

Dieter Hellwinkel[a]; Heinz Stahl[a]; Heinrich Georg Gaa[a]; Reiner Gottfried[a]
[a] Organisch-Chemisches Institut der Universität Heidelberg, Deutschland

To cite this Article Hellwinkel, Dieter , Stahl, Heinz , Gaa, Heinrich Georg and Gottfried, Reiner(1983) 'Novel Colored Systems of the "Inverted Triphenylmethylium Dye" Type Containing Nitrogen, Phosphorus, Sulfur and Congeneric Donor Centers', Phosphorus, Sulfur, and Silicon and the Related Elements, 18: 1, 121 — 124

To link to this Article: DOI: 10.1080/03086648308075982

URL: http://dx.doi.org/10.1080/03086648308075982

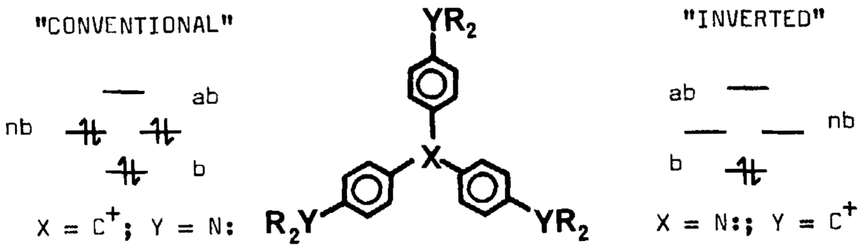
Phosphorus and Sulfur, 1983, Vol. 18 pp. 121-124
0308-664X/83/1801-0121/$18.50/0

NOVEL COLORED SYSTEMS OF THE "INVERTED TRIPHENYLMETHYLIUM DYE" TYPE CONTAINING NITROGEN, PHOSPHORUS, SULFUR AND CONGENERIC DONOR CENTERS

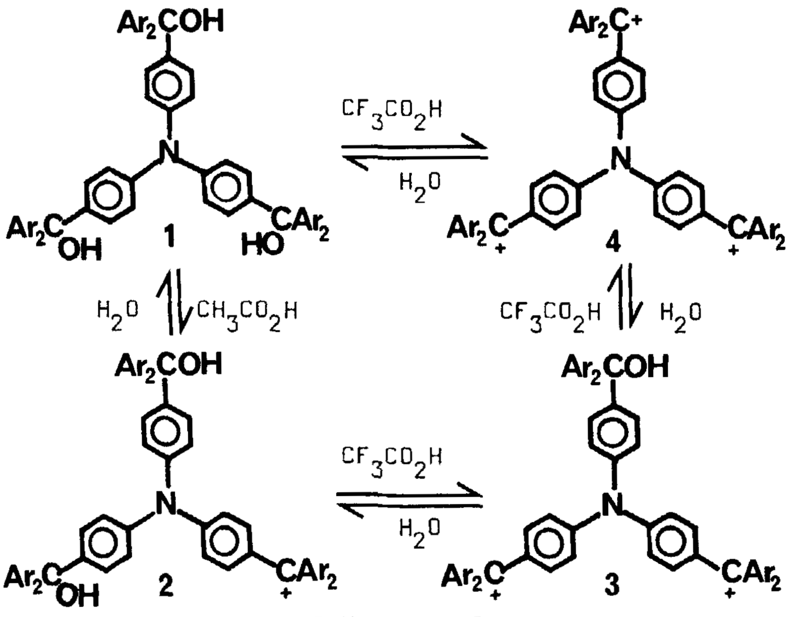
DIETER HELLWINKEL, HEINZ STAHL, HEINRICH GEORG GAA AND REINER GOTTFRIED
Organisch-Chemisches Institut der Universität Heidelberg, Deutschland

In the course of a fundamental study relating to the question of color and constitution it was found, that a simple HMO-treatment of the isoconjugate resonance system of triphenylmethylium (TPM) dyes[1] provides a very variegated scenery for imagining some novel dye systems. Thus, for the archetype of all TPM-dyes, crystal violet, the spectroscopically relevant frontier orbitals show above a core of nine bonding MO's with a limiting energy of ß, two nonbonding levels (nb), one slightly bonding (b) and one slightly antibonding (ab) MO, respectively. The occupancy of the frontier orbitals is 6, so that the longest wavelength absorption corresponds to an excitation from a nb-MO to the weakly antibonding MO. One sees at once, that diminuation of the frontier orbital occupancy by 4, leaving only 2 electrons, should generate a new dye system presenting approximatly the same color as crystal violet, since now the longest wavelength absorption would correspond to a transition from the (symmetrically situated) slightly bonding MO to a nb-MO.

This idea appeared easily realizable by an inversion of functionalities, that is, by placing the nitrogen donor in the middle and the three carbenium acceptors at the periphery of the model system. This should give rise to a new dye system which could be defined in terms of an "inverse crystal violet" type and which appeared very appropriate for a systematic study of the conjugational abilities of quite a variety of donor centers such als P, S and their congeners of the V. and VI. main groups of elements.

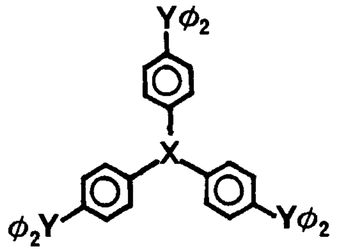


We first studied those systems comprising a central nitrogen donor, and, for the sake of stability, a completely arylated periphery[2]. The experiments revealed indeed a broad spectrum of fascinating color phenomena.

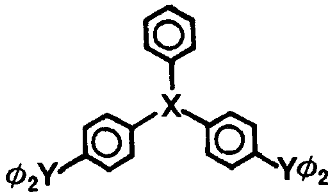


$Ar = C_6H_5, p\text{-}CH_3C_6H_4$

Depending on the strength of the acid solvents used, tris-carbinol **1** (or a corresponding tris-ether) could be transformed reversibly into the violet mono-carbenium-ion **2**, the dull green bis-ion **3** or the bright green tris-ion **4**. That the principle of "Color Retention by Functionality Inversion" has operated nearly perfectly here is demonstrated by the direct comparison of corresponding "conventional" and "inverted" dye types, which in fact have each nearly the same color and longest wavelength absorption.

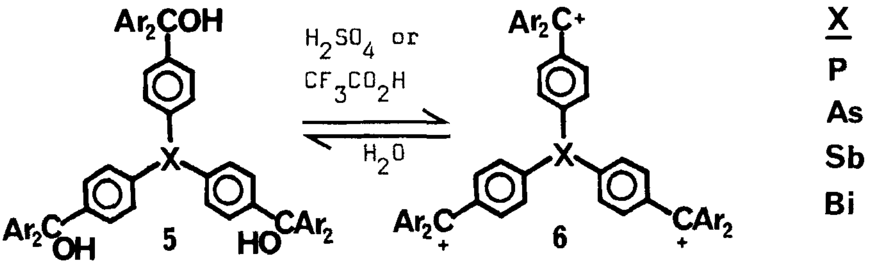


X = C^+ ; Y = N: 630 nm
X = N: ; Y = C^+ 637 nm



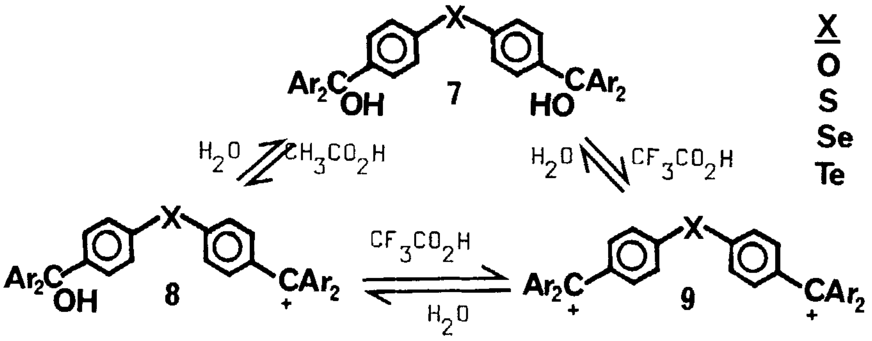
X = C^+ ; Y = N: 670 nm
X = N: ; Y = C^+ 674 nm

With phosphorus as central donor the situation was rather undecided as it is known, that a donor capacity of the free electron pair in the inherently pyramidal triarylphosphines is generally not perceptible[3]. But we hoped that the combined pulling forces of three peripheral carbenium functions would enforce conjugation through, and flattening of, the whole system. For testing this, the following model 5 was chosen.



Dissolving tris-carbinol 5 (or a corresponding tris-ether) in strong acids produced orange-red solutions with a relatively constant λ_{max} of around 465 nm. Since this value equals more or less that of the simple tris-p-tolylmethylium-ion (452 nm), we have to conclude that all the cationic species derived from 5, and even the tris-cation 6, represent in fact trivial multiple tritylium systems connected by an essentially isolating and only inductively acting trivalent phosphorus. Comparable results were obtained with analoguous As, Sb and Bi compounds.

Contrary to this, central atoms of main group VI always have a conjugation-prone free p-electron pair which can interact with adjacent π-systems[4]. Consequently, the bis-carbinols 7, when dissolved in strong acids, exhibit again bright colors, ranging from red-orange for Z = O, violet for Z = S, to blue-violet and green for Z = Se and blue-green for Z = Te. Here again this speaks for the new dye systems 9 (and 8) representing essentially the "inverted malachite green" type[5].



REFERENCES

1. J.Fabian and H.Hartmann, Light Absorption of Organic Colorants, (Springer-Verlag, Berlin, 1980), p 138.
2. F.Strohbusch and H.Zimmermann, Tetrahedron Lett. (1969), 1705.
3. B.E.Mann, J.Chem.Soc., Perkin Transact. II, (1972), 30; G.P. Schiemenz, Tetrahedron Lett. (1964), 2729. R.Batchelor and T.Birchall, J.Am.Chem.Soc. 104, 674 (1982).
4. R.Wizinger-Aust, Quart.Rep. Sulfur Chem. 5, 191 (1970).
5. W.Dilthey, L.Neuhaus, E.Reis and W.Schommer, J.Prakt.Chem. 124, (232), 81, 100 (1929).