

**This Week's Citation Classic**<sup>®</sup>

Merrifield R E & Phillips W D. Cyanocarbon chemistry. II. Spectroscopic studies of the molecular complexes of tetracyanoethylene.  
*J. Amer. Chem. Soc.* **80**:2778-82, 1958.  
[Central Research Dept., Experimental Station, E.I. du Pont de Nemours & Co., Wilmington, DE]

Spectroscopic data and complex-formation equilibrium constants are reported for some two dozen charge-transfer complexes of tetracyanoethylene (TCNE) with a variety of electron donors—mostly aromatic hydrocarbons. TCNE is found to be the strongest pi-electron acceptor yet reported. [The *SCI*<sup>®</sup> indicates that this paper has been cited in over 405 publications since 1958.]

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This paper was the second of a group of 12 papers with a total of 21 different authors that were published in the same issue of the *Journal of the American Chemical Society*.<sup>1-11</sup> These papers announced the synthesis of tetracyanoethylene (TCNE), the first example of a percyanoolefin, and reported on its exceedingly rich chemistry and on its unusual physical properties. Among the latter was the formation of intensely colored solutions in aromatic hydrocarbon solvents.

When I first came to DuPont in 1953, an extensive research program on cyanocarbon chemistry had been under way for some

time. Bill Phillips had started a study of the charge-transfer complexes of TCNE, which were responsible for the aforementioned colors. My initial assignment was to continue this study, which entailed spectroscopic measurements of the complex-formation equilibrium constants and heats of formation as well as investigation of steric and solvent effects. This was an ideal project for a freshly minted physical chemist trained in molecular spectroscopy. Not least among the pleasures of this research were the surprising and delightful colors of each new complex, although the delight was frequently short-lived as the strongly dienophilic nature of TCNE asserted itself, and the complex transformed into a colorless Diels-Alder adduct. In addition to our quantitative results on the complexes, the principal conclusion of this work was that TCNE was by far the strongest pi-electron acceptor examined up to that time.

Although research on cyanocarbon chemistry continued at DuPont for several more years, Phillips and I both moved on to other areas after the work reported in this paper—he to nuclear magnetic resonance and I to the physics of molecular crystals. We were both to return to the subject of cyanocarbons some time later with the discovery of tetracyanoquinodimethane (TCNQ) and its highly conducting ion-radical salts.<sup>12</sup>

I am not sure why this paper has been highly cited. Neither the experimental methods employed nor the theoretical interpretations invoked were particularly novel! Most likely it is because of the unique nature of TCNE and the unusual properties of cyanocarbons in general.

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