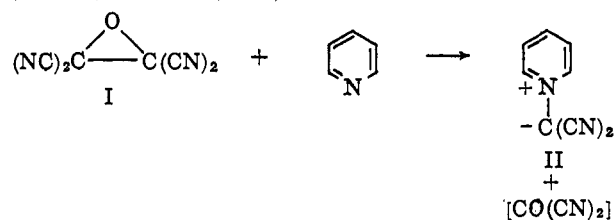
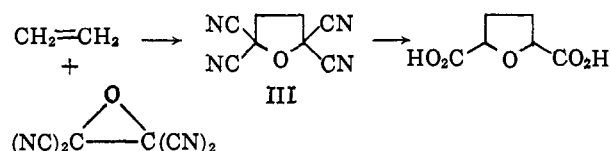


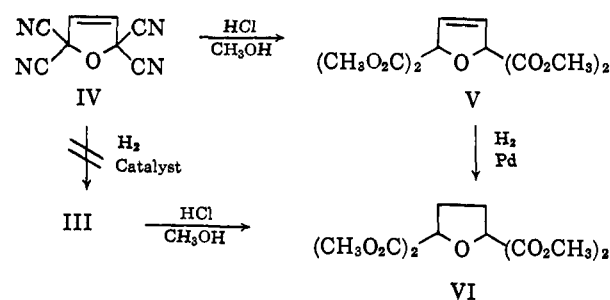
ylide II, m.p. 245–246°, is obtained in 80% yield. (*Anal.* Calcd. for $C_8H_5N_3$: C, 67.14; H, 3.52; N, 29.37; mol. wt., 143. Found: C, 67.30; H, 3.61; N, 29.43; mol. wt., 142).



The most striking reaction of TCNEO is the addition to olefinic and acetylenic compounds to give tetracyano-tetrahydro- and tetracyanodihydrofurans, respectively. Ethylene and TCNEO condense smoothly at 130° to give 2,2,5,5-tetracyanotetrahydrofuran (III), m.p. 107–108°, in 87% yield (*Anal.* Calcd. for $C_8H_4N_4O$: C, 55.84; H, 2.34; N, 32.56; mol. wt., 172. Found: C, 56.05; H, 2.50; N, 32.52; mol. wt., 184.) The ethylene adduct shows an unsplit proton resonance at 6.68 τ and is hydrolyzed with partial decarboxylation to the known tetrahydrofuran-*cis*-2,5-dicarboxylic acid.³

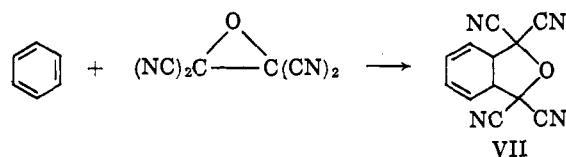


Under similar conditions, acetylene and TCNEO give 2,2,5,5-tetracyanodihydrofuran (IV), m.p. 160–161°, in 71% yield (*Anal.* Calcd. for $C_8H_2N_4O$: C, 56.50; H, 1.19; N, 32.96. Found: C, 56.73; H, 1.22; N, 32.54.)



It has not yet been possible to reduce IV to III catalytically, but IV has been converted to the corresponding tetraester V,⁴ m.p. 96.5–97°. Catalytic reduction of V gives the saturated ester VI,⁴ m.p. 103–104°, which is identical with that synthesized from III.

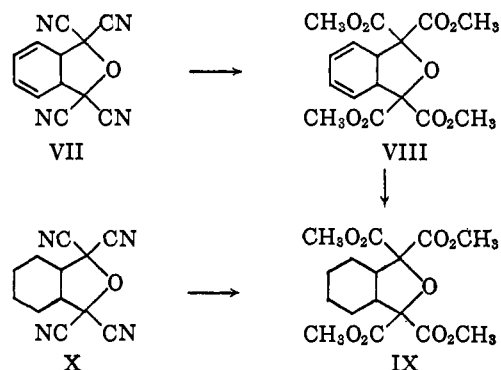
TCNEO also adds to aromatic systems, such as benzene and *p*-xylene, with surprising ease to form tetrahydroisobenzofurans.



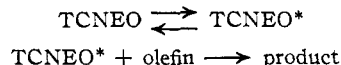
The monoadduct with benzene, 1,1,3,3-tetracyano-1,3,3a,7a-tetrahydroisobenzofuran (VII), m.p. 167–168° (*Anal.* Calcd. for $C_{12}H_8N_4O$: C, 64.84; H, 2.72; N, 25.21; mol. wt., 222. Found: C, 64.95; H, 2.87; N, 24.68; mol. wt., 228), is isolated in 35%

yield when TCNEO is heated in excess benzene at 130–150°.

The tetrahydroisobenzofuran VII shows an ultraviolet absorption spectrum typical of a 1,3-cyclohexadiene (λ_{max} 259 $m\mu$, ϵ 3800 in CH_3CN). The adduct VII is converted with hydrogen chloride-methanol to a tetraester VIII,⁴ m.p. 93.5–94.5°, that is reduced to a saturated tetraester IX,⁴ m.p. 114–115°. This latter product is identical with the tetraester derived from the adduct X of cyclohexene with TCNEO.



A kinetic study of the addition of TCNEO to styrene and to substituted stilbenes strongly indicates that the reaction involves preliminary promotion of TCNEO to an activated species. With a sufficiently reactive olefin, this step is rate-controlling.



Other polycyano olefins have also been epoxidized by hydrogen peroxide in acetonitrile with retention of the nitrile groups.⁵ The following oxides have been prepared by this method: phenyltricyanoethylene oxide, m.p. 78–80° (72% yield) (*Anal.* Calcd. for $C_{11}H_5N_3O$: C, 67.69; H, 2.57; N, 21.54. Found: C, 68.04; H, 2.89; N, 21.45), tricyanoethylene oxide, m.p. 76–77° (31% yield) (*Anal.* Calcd. for $C_5H_3N_3O$: C, 50.42; H, 0.85; N, 35.29. Found: C, 50.47; H, 0.90; N, 35.52), *t*-butyltricyanoethylene oxide, m.p. 44–45° (76% yield) (*Anal.* Calcd. for $C_9H_9N_3O$: C, 61.70; H, 5.18; N, 23.99. Found: C, 61.88; H, 5.41; N, 24.03) and 1,2-bis-(ethoxycarbonyl)-1,2-dicyanoethylene oxide, m.p. 61–70° (93% yield) (*Anal.* Calcd. for $C_{10}H_{10}N_2O_5$: C, 50.41; H, 4.23; N, 11.76. Found: C, 50.61; H, 4.25; N, 12.09). A catalytic amount of base, such as pyridine, may be used to increase the rate of epoxidation of these olefins.

(5) Epoxidation of α,β -unsaturated nitriles with alkaline hydrogen peroxide has previously led predominantly to the corresponding epoxyamide. See G. B. Payne and P. H. Williams, *J. Org. Chem.*, **26**, 651 (1961). Amide formation has been avoided by epoxidizing with an alkyl hydroperoxide [G. B. Payne, *ibid.*, **26**, 663 (1961)] or hypochlorite ion [D. H. Rosenblatt and G. H. Broome, *ibid.*, **28**, 1290 (1963)].

CONTRIBUTION NO. 883
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RECEIVED MAY 27, 1963

A Stable Triplet State of Pentaphenylcyclopentadienyl Cation

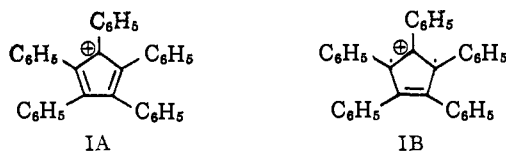
Sir:

It is predicted by molecular orbital theory that cyclopentadienyl cation, or a derivative of it which retains the fivefold symmetry, could be a triplet in its ground state. Such a prediction is made for many other symmetric systems with $4n$ π -electrons, e.g. cyclobutadiene,

(3) A. C. Cope and W. N. Baxter, *J. Am. Chem. Soc.*, **77**, 393 (1955).

(4) Satisfactory analytical data have been obtained.

and it is based on considerations, for molecular orbitals, analogous to those which lead to Hund's rule for atoms. However, for pentaphenylcyclopentadienyl cation (I) and other molecules of this type the prediction is not unambiguous, since the improved electron-repulsion energy in the triplet is counter-balanced by Jahn-Teller stabilization of the singlet.¹ We have reported previously that heptaphenylcycloheptatrienyl anion is a singlet.² Furthermore, the tetrapotassium salt of tetrahydroxybenzoquinone is a singlet³; if the anion were not coordinated with potassium ions, it too would be a potential triplet. Several species have recently been described⁴ in which two unshared electrons do unpair to give a triplet ground state, but the type of system we are considering is of particular interest since the prediction is that a *bond*, in valence bond terms, will be broken by electron unpairing. The only previous⁵ examples of such situations are O₂ and S₂. We now wish to report that we have prepared pentaphenylcyclopentadienyl cation (I), and that this species is to a significant extent present as a triplet, which may be represented in valence bond terms as IB and its resonance forms.



Reaction of pentaphenylcyclopentadienol⁶ (II) with sulfuric acid leads to the desired cation only fleetingly, since it rearranges in a few seconds to triphenylcyclopentadienophenanthrene and other products.⁷ However, when BF₃ is passed through a solution of II in methylene chloride at -60°, a deep blue solution results, containing the cation I. If this solution is quenched in cold methanol, a 90% yield of the expected methyl ether, m.p. 197-198°,⁸ is obtained, identical with an authentic sample (from a Williamson synthesis using II and methyl iodide). After 1 hr. at -78° an 87% yield of the ether is still formed on quenching. If a twofold excess of cycloheptatriene is added to the cold solution before quenching, however, pentaphenylcyclopentadiene is now obtained in 98% yield, resulting as expected from hydride transfer to the unstable carbonium ion.

An n.m.r. spectrum of a 0.13 M solution of I in CH₂Cl₂ at -60° shows a broadened solvent line and no trace of absorption from the phenyl hydrogens. The same observation is made with solutions in SO₂ or in BF₃·etherate. By contrast, a 0.13 M solution of II in methylene chloride, to which diphenylpicrylhydrazyl has been added, shows phenyl protons as well as solvent protons, both commensurately broadened by paramagnetic relaxation effects.^{2,7,9} Accordingly, all the phenyl protons in our cation solution are in molecules

which are paramagnetic themselves, either permanently or transiently. It seemed that I was either predominantly the triplet IB or an equilibrium mixture of IA and IB; singlet-triplet interconversion can be rapid in the presence of other paramagnetic species. This conclusion was confirmed by e.p.r. studies.

A 0.065 M solution of I in CH₂Cl₂ was frozen to 77°K. and the microcrystalline mass was examined by previously reported techniques.¹⁰ A signal was found for a $\Delta m = 2$ transition at 1482 gauss, and $\Delta m = 1$ satellites were found at 2611 and 3753 gauss. These signals unambiguously demonstrate the presence of a triplet. The value of D for this species is 0.1050 cm.⁻¹, while E is found to be zero. The D -value, which measures the interaction of the two unpaired electrons, is similar to that found for some organic (excited state) triplets of similar size¹¹; the value of E shows that the spin-spin interaction is isotropic in the xy plane, as is expected for a system with C₅ or greater symmetry. There is also present a signal at $g = 2$ which we assign to contamination by a cation radical of a rearrangement product.⁷

The spectrum was examined over the temperature range 77°K. to 136°K., with power levels such that no saturation was occurring, and a reversible over-all 60% increase in the $\Delta m = 2$ signal was observed at the higher temperature, with a similar change in the $\Delta m = 1$ satellites. After correction by the Curie law, these data reveal that the triplet is 0.48 ± 0.05 kcal./mole above the ground state of the system. It would be simplest to conclude that the ground state of I is the singlet IA, with the triplet IB being slightly above it. However, since these measurements are performed in the solid state, we cannot exclude the possibility that the equilibrium being observed actually involves I (as its triplet) and some other singlet species, e.g., an ion pair of I. Accordingly it is possible that in solution I exists entirely as the triplet IB; in any case our data show that this species is at least comparable in energy with the singlet. Including statistical weights, the energy difference observed means that at least 50% of I would be the triplet IB at -60°, with more at higher temperatures.

If the solution of I is warmed to room temperature, a rearrangement and color change occur. Quenching no longer affords any methyl ether derived from I, but instead a complex mixture is obtained which has not been fully identified. Furthermore, when the rearranged solution is frozen to 77°K., the $\Delta m = 1$ satellites and the $\Delta m = 2$ line in the e.p.r. have disappeared, while the monoradical signal is even stronger.

It thus is clear that electron correlation effects¹² have largely overcome other factors in I. However, there is apparently a delicate balance in such systems, and experimental evidence must be supplied for any new compound of this type before it can be concluded that it also has a stable triplet state.¹³

(1) Calculations on several such species are reported by L. Snyder, *J. Phys. Chem.*, **66**, 2299 (1962).

(2) R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **84**, 1484 (1962).

(3) R. West and H. Niu, *ibid.*, **84**, 1324 (1962).

(4) (a) R. W. Murray, A. M. Trozzolo, E. Wasserman and W. A. Yager, *ibid.*, **84**, 3213 (1962); (b) G. Smolinsky, E. Wasserman and W. A. Yager, *ibid.*, **84**, 3220 (1962); (c) A. M. Trozzolo, R. W. Murray and E. Wasserman, *ibid.*, **84**, 4990 (1962); (d) R. W. Brandon, G. L. Closs and C. A. Hutchison, Jr., *J. Chem. Phys.*, **37**, 1878 (1962).

(5) G. Hoihtink, *Mol. Phys.*, in press, recently has detected the triplet state of the dianion of *s*-triphenylbenzene.

(6) K. Ziegler and B. Schnell, *Ann.*, **445**, 266 (1925).

(7) R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 3727 (1961).

(8) C. Dufraisse, A. Etienne and J. Aubry, *Compt. rend.*, **239**, 1170 (1954), report m.p. 198-199°.

(9) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y. 1959, p. 207 ff.

(10) W. A. Yager, E. Wasserman and R. M. R. Cramer, *J. Chem. Phys.*, **37**, 1148 (1962).

(11) J. H. van der Waals and M. S. deGroot, *Mol. Phys.*, **3**, 190 (1960). Systems⁴ in which the spins are more localized on one atom have larger values of D .

(12) A simple m.o. calculation, assuming a ring-phenyl angle of 60°, shows that the two electrons of the degenerate pair of orbitals will be 72% localized on the cyclopentadienyl ring.

(13) Partial support of this work by a grant from the National Science Foundation and helpful comments by Dr. E. Wasserman are gratefully acknowledged.

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