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TWO NEW INERT CARBON BIRADICALS OF THE TRIPHENYLMETHYL SERIES. SYNTHESIS, CONFORMATION AND SPIN EXCHANGE

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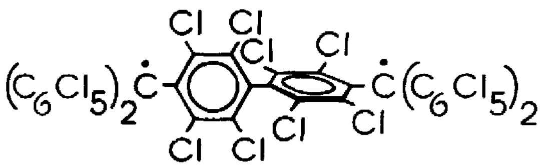
Summary: The synthesis and some properties of two new "chemically inert" free biradicals, the perchloroethynylene- (III) and perchlorovinylenebis-4-triphenylmethyl (IV), are described. They correspond to hydrocarbon analogues known to exist, at least predominantly, in a singlet, quinonoid form.

Perchloro-α, α, α',α'-tetraphenylbi-p-tolyl-α ,α'-ylene (PTBT) is the only chlorocarbon biradical described in detail so far.[1] Uv-vis., epr and magnetic susceptibility measurements indicate that its two identical halves are electronically independent since, on account of the repulsions among the four central ortho-chlorines, the two biphenyl benzene rings are about perpendicular.

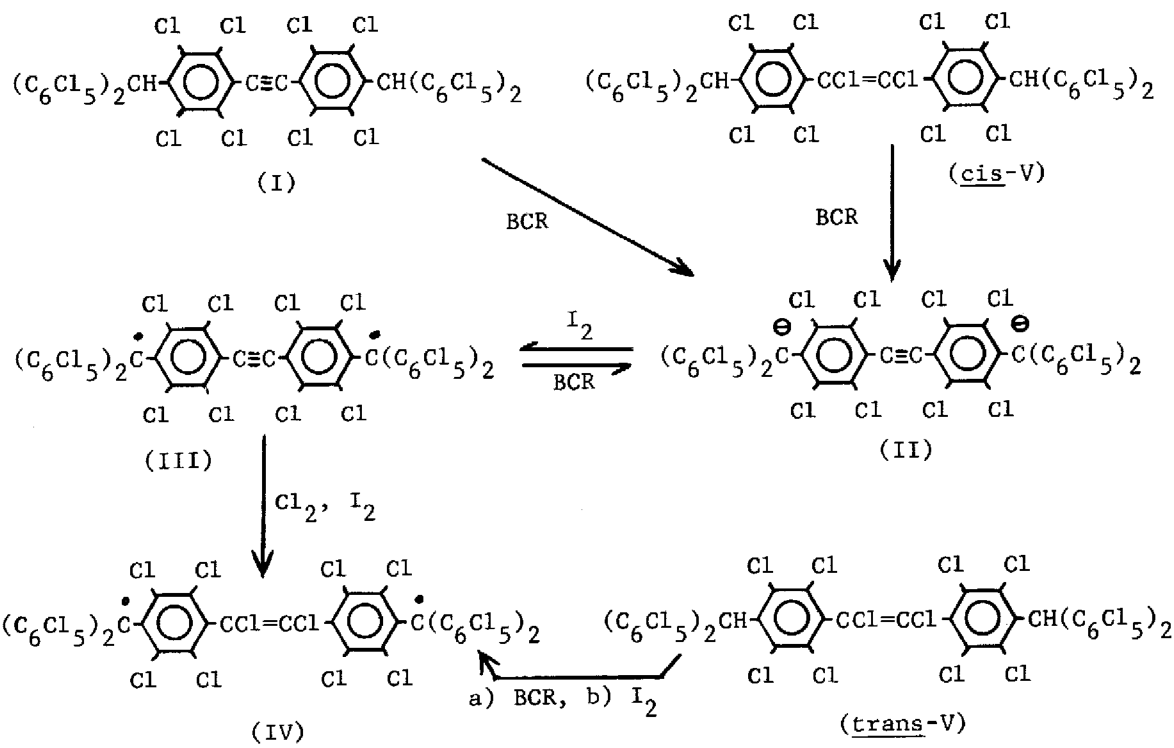


(PTBT)

Two new inert paramagnetic chlorocarbons, possessing some unusual features, are here reported. Treatment of αH,α'H-octacosachloroethynylenebis-4-triphenylmethane (I)[2] with reagent BCR (NaOH-ether-DMSO),[1] followed by oxidation with I_2 of the resulting deep-blue solution of dicarbanion (II), gives perchloroethynylenebis-4-triphenylmethyl (III) (77.4%), a green chlorocarbon biradical melting at 334-6º (dec). IR (KBr) ν 1510 (w)(1rst arom.), 1424 (w), 1333 (s)(2nd arom.), 1260 (m), 810 (m), 730 (m), 710 (s), 660 (m), 645 (m) and 530 (m) cm^{-1}. Uv-vis (C_6H_{12}) λ (ε) 222 (150,000), 296 (17,100; sh), 385 (53,200), 435 (22,700), 460 (27,900) and 637 (41,300) nm. EPR (CCl_4) g, 2.0027 ± 0.0003; singlet, width 1.2 G; a(α-^{13}C) 28.3, a(bridgehead-^{13}C) 12.2, a(o-^{13}C) 10.2 G.

Since the magnetic susceptibility of this biradical is about as half the theoretical value, being its variation with temperature anomalous, its chemical purity was ascertained indirectly: (III) in CCl_4, at room temperature, reacts with Cl_2 in the presence of I_2 giving a 94.4% yield of biradical trans-perchlorovinylenebis-4-triphenylmethyl (IV), a red chlorocarbon melting at 354-6º (dec). IR (KBr) ν 1512 (w)(1rst arom.), 1340 (s)(2nd arom.), 1327 (s)(idem.), 1260 (m), 1165 (m), 820 (m), 815 (s), 730 (m), 700 (m), 650 (m), 530 (m) and 500 (m) cm^{-1}. Uv-vis (C_6H_{12}) λ (ε) 222 (164,000), 290 (13,500; sh), 340 (12,300; sh), 368 (35,400; sh), 388 (74,500), 510 (2430) and 563 (2340) nm. EPR ($CHCl_3$) g, 2.0028 ± 0.0003; singlet, width 2.15 G; a(α-^{13}C) 13.9, a(arom-^{13}C) 5.0 G. Magn. suscept. χ_{dia} $-0.463\cdot10^{-6}$ emu, θ 4.0ºK, Bohr magn. 2.43 (98% pure), spins/mole, $11.8\cdot10^{23}$. The chemical purity of (III) is therefore at least 92.5%.

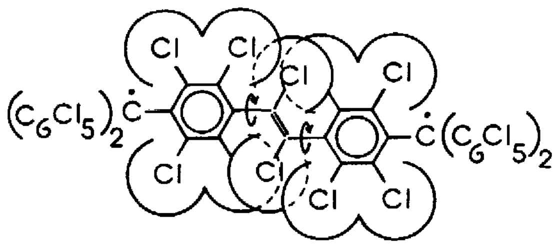
(III) can also be obtained from cis- αH,α'H-triacontachlorovinylenebis-4--triphenylmethane (cis-V)[2] by treatment with reagent BCR, followed by oxidation with I_2 (35.8%).



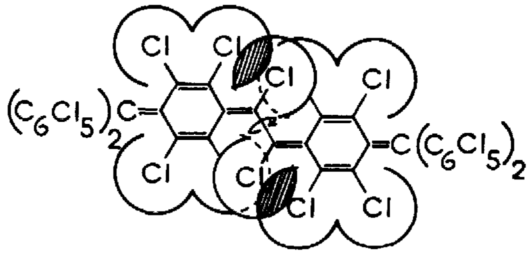
Treatment of trans- αH,α'H-triacontachlorovinylenebis-4-triphenylmethane (trans-V)[2] with reagent BCR followed by oxidation with I_2 gives a mixture containing about 2/3 of ethylene biradical (IV), the rest being acetylene (III). By reduction of this mixture with reagent BCR and subsequent acidification, a mixture of the αH-quasiperchlorocompounds (trans-V) and (I) is obtained. In this connection it is mentioned that by this treatment biradical (III) affords αH, α'H-quasiperchlorocompound (I) (62.9%).

Variation of magnetic susceptibility of solid acetylene (III) with temperature takes place as if it were in equilibrium with a diamagnetic species, the lower the temperature the higher the proportion of the latter.

Like biradical (PTBT), ethylene biradical (IV) cannot exist in the singlet, quinonoid form (VI) on account of the great steric strain in the all-planar conformation. This strain is caused by the repulsions between the two central chlorines and the four proximal ortho-chlorines.[3-5] Nevertheless, the space-filling scale atomic models indicate that in the most favoured conformation the π-electron systems of the two halves are not at right angles as in (PTBT) but just tilted with respect to the ethylene system and, consequently, the π-electron interactions between the two identical moieties do exist. In fact, biradical (IV)



(IV)



(VI)

behaves as a triplet in the epr, since the values of the coupling constants with the α-^{13}C (13.9 G) and the arom-^{13}C (5.0 G) are about half of those for closely related monoradicals, such as perchlorotriphenylmethyl (PTM; 29.5, and 12.5-10.7 G),[1] or biradical (PTBT) (29.1, and 9.7 G),[1] as predicted for cases involving one magnetically active nucleus with spin 1/2 and one inactive nucleus.[6]

Since the epr spectrum of acetylene biradical (III) in solution shows a normal ^{13}C splitting (28.3 G), it may be inferred that it is, at least partly, in the perpendicular conformation.[7,8]

All biradicals here described analyse correctly for C and Cl. As in other triphenylmethyl chlorocarbon radicals,[1] they are completely disassociated because of the colossal steric strain that their dimers or polymers would possess.

Also, steric shielding of their tricovalent carbon atoms is so effective that the latter are inert towards oxygen, and in reactions that would involve those atoms, such as the chlorination of actylene (III), were the radical character remains quantitatively undisturbed. Nevertheless, they are active in electron--transfer processess, as shown by their reduction with reagent BCR.

It is pointed out that the hydrocarbon analogues of acetylene (III)[9] and e-thylene (IV)[10] (Wittig hydrocarbon[11]) are most predominantly in their quinonoid (singlet) forms, being air-sensitive and highly reactive.

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