

LIGHT-INDUCED RING CLOSURE IN THE PERCHLORO-TRIPHENYLMETHYL RADICAL

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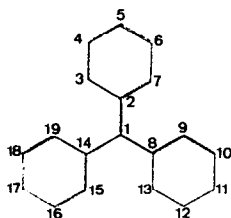
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The solution electron resonance spectrum of the perchloro-triphenylmethyl radical (PTM) consists of a single line, together with two pairs of carbon-13 satellites. On the basis of molecular orbital calculations, the 31.9 MHz splitting was attributed to the central carbon atom (position 1) and the second (30.0 MHz) to the three bridgehead carbons (positions 2, 8 and 14) and the six ortho carbons (positions 3, 7, 9, 13, 15 and 19)<sup>1</sup>. Solutions of PTM are photosensitive and change from orange to green. This is accompanied by the broadening of the central electron resonance line and only a single <sup>13</sup>C splitting, 52.3 MHz, is observed. The photo-decomposition is irreversible and the radical product, in the absence of oxygen, is stable for many months. The satellite lines are 224 times weaker than the central line, and must therefore be caused by a single carbon atom in the radical.



The change in the optical absorption spectrum of the radical is consistent with a photo-induced ring closure leading to greater delocalization of the unpaired electron. Reactions of the type leading to the formation of a bond between, for example, atoms 7 and 9, though not common, are known<sup>2</sup>. For PTM, however, three ring closures are theoretically possible, but it is not obvious which of the possible products would be most stable. If this proposal is correct, then

the single  $^{13}\text{C}$  splitting must be assigned to the central carbon atom of the radical. In order to determine how many ring closures occur we have calculated the  $^{13}\text{C}$  hyperfine splittings for the three possible products, and conclude that only one bond is formed.

Although the practice of comparing experimental values with coupling constants calculated from Hückel or McLachlan spin densities, using the McConnell relationship<sup>3</sup> for protons and the Karplus and Fraenkel relationship<sup>4</sup> for carbon- $^{13}\text{C}$  nuclei, is well established, one should be aware of the limitations in using this method to distinguish between possible structures. The exact form of the relationship between coupling constants and spin densities is still under discussion<sup>5</sup> and a range of semi-empirical spin polarisation constants,  $Q$ 's are in use. When choosing a structure on the basis of calculated spin densities one must therefore ensure that a slightly different choice of parameters would not favour an alternative structure.

The position is, of course, even more complicated when hetero-atoms are present, since it is necessary to introduce parameters, Coulomb and resonance integrals, whose values<sup>6</sup> are often determined by little more than intuition. In PTM, however, there are no hetero-atoms in the basic molecular skeleton, so the basic set of atomic orbitals contains only carbon  $2p_z$  orbitals, provided we neglect the electron pairs in the chlorine orbitals. The values chosen for the parameters were:

(i) To allow for the inductive effect of chlorine we write for the adjacent carbon atoms

$$\alpha' = \alpha + 0.2\beta,$$

and small variations in the inductive parameter are not critical.

(ii) If more than one ring closure occurs the radical is forced into a planar configuration, but when only one ring closure takes place one phenyl ring is free to rotate and we write

$$\beta_{1,14} = \beta \cos \theta,$$

where  $\theta$  is the angle between the central carbon  $2p_z$  orbital and the  $2p_{\pi}$  orbital on the ring.

(iii) The resonance integrals for the new bonds were set equal to  $0.9\beta$ .

McLachlan spin densities were calculated for the radicals produced by one, two and three ring closures, and the results of these calculations are given in the table 1. It is apparent that  $\rho_1$  does not depend critically on the value of  $\theta$ .

Although we have allowed for the inductive effect of the chlorine atoms, neglect of their conjugation with the carbon  $\pi$ -system may lead to errors in the spin density distribution. However, the results of a calculation, for PTM, which

Table 1. Results of Molecular Orbital Calculations

	Spin Densities						<sup>13</sup> C Coupling Constant (MHz)					
	Central		Bridge head		Ortho		Central		Bridge head		Ortho	
	$\rho_1$	$\rho_2$	$\rho_{14}$	$\rho_{19}$	$\rho_3$	$\rho_{19}$	$a_1$	$a_2$	$a_{14}$	$a_3$	$a_{19}$	$a_{19}$
PTM (1 ring closure) formation of bond 7 - 9												
$\theta = 50^\circ$	0.4917	-0.0469	-0.0279	0.0495			46.93	31.75	25.43	0	0	14.4
$\theta = 60^\circ$	0.5166	-0.0505	-0.0189	0.0306			49.00	33.33	24.16	0	0	19.3
$\theta = 70^\circ$	0.5381	-0.0538	-0.0098	0.0145			50.75	34.69	22.96	0	0	23.7
$\theta = 80^\circ$	0.5527	-0.0563	-0.0027	0.0038			51.92	35.62	22.08	0	0	26.8
PTM (2 ring closures) formation of bonds 7 - 9 and 3 - 19												
	0.4209	-0.0146	-0.041				39.88	24.65	27.64	0	0	0
PTM (3 ring closures) formation of bonds 7-9, 13-15 and 3-19												
	0.4395	-0.0281					41.00	26.94		0	0	0

includes the chlorine 2p orbitals is in good agreement with that using an inductive parameter. The spin densities quoted in the table can now be used with some confidence to calculate the  $^{13}\text{C}$  splittings from<sup>4</sup>

$$a_1^{\text{C}} = 85.8 \rho_1^{\text{C}} - 39.0 \sum_{i=1}^3 \rho_i^{\text{C}} \text{ (MHz)}$$

We realise that the numerical coefficients were determined for hydrocarbons, and not for chlorocarbons, but in no case is there a chlorine atom as nearest neighbour to the carbon atoms of interest and in any case we have no alternative but to use these values. Twisting of the rings causes the  $2p_z$  orbital on the central carbon to overlap directly with the ortho carbons, and so produces a splitting which is given by<sup>1</sup>:

$$a = 150 \sin^2 \theta \text{ (MHz)}.$$

The carbon-13 splittings calculated from these equations are given in the table. The spin density on the central carbon atom, and thus the larger  $^{13}\text{C}$  coupling, decreases as first one and then two ring closures occur. After two or three ring closures the spin density remaining on the central carbon atom is much too small to account for the observed coupling of 52.3 MHz, for the calculated coupling constants are only 40 MHz. However, the calculated  $^{13}\text{C}$  splitting for the radical resulting from a single ring closure increases with increasing  $\theta$  and is about 50 MHz for values of  $\theta$  greater than the  $60^\circ$  found in PTM. In all three radicals the calculated couplings to the bridgehead and ortho positions are less than 36 MHz and would be hidden under the wings of the central line. We conclude, therefore, that the product formed by photo-decomposition of PTM is the perchloro-9-phenylfluorenyl radical.

We are grateful to Professor Ballester for donating the perchloro-triphenylmethyl radical whose preparation is reported elsewhere<sup>7</sup>.

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