The Dipole Moments of Octachloropentafulvalene, Hexachloropentafulvene, and Related Substances[1]

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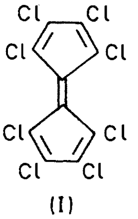
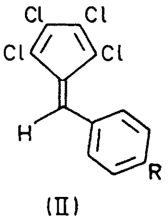
Summary Significant dipole moments have been observed for octachloropentafulvalene, hexachloropentafulvene, 1,2-dichloro-3,4-bis(dichloromethylene)cyclobutene, and a few 6-aryl-1,2,3,4-tetrachloropentafulvenes in solution, indicating in some cases, the ability of these chlorocarbons to form molecular complexes with the solvent.

ADVANCES made in the series of cyclic conjugated chlorocarbons have established the independent status[2,3] of chlorocarbon chemistry. The unique properties of these systems have been illustrated by the case of octachloropentafulvalene (I).[4,5] Recently, West has shown,[3,6] *inter alia*, that (I) forms excited-state charge-transfer complexes with aromatic hydrocarbons. The spatial structure of (I) has been determined directly by *X*-ray crystallography[7] and circumstantially by n.q.r. spectroscopy.[8] We now report the significant dipole moments of (I) and a series of related chlorocarbon systems.[9]

In spite of the high symmetry of its formula, (I) has in benzene a dipole moment of 0·95 D ($\alpha' = 2\cdot19, \beta' = -3\cdot17$, $P_{2\infty} = 97\cdot1$ cm^3, MR$_{\text{calc}} = 78\cdot7$ cm^3). This value may be attributed to a molecular complex of (I) with the solvent. It is likely that the interactions involved are of a charge-transfer character. In cyclohexane, in which no such complexes can be formed, the very small moment of 0·40 D ($\alpha' = 1\cdot69$, $\beta' = -3\cdot89$, $P_{2\infty} = 82\cdot1$ cm^3) was found. This interpretation is supported by the high dipole moment in mesitylene, 1·58 D ($\alpha' = 2\cdot47$, $\beta' = -1\cdot90$, $P_{2\infty} = 129\cdot4$ cm^3): mesitylene is a better donor than benzene for the formation of charge-transfer complexes.[10,11]

Differences between the solutions in benzene and cyclohexane were also observed in the measurement of the dipole moments of some 6-aryl-1,2,3,4-tetrachloropentafulvenes (II).[12] The dielectric constants of 1,2,3,4-tetrachloro-6-(*p*-chlorophenyl)pentafulvene (II; R = Cl) and of the 6-(*p*-fluoro-phenyl)-compound (II; R = F) in benzene were not a linear function of the concentration; in cyclohexane, they are linear and the experimental dipole moments are 1·78 and 1·63 D, respectively. In cases where the dipole moment to be expected is relatively small, the complex formation with benzene has an appreciable effect on the dielectric constant. Indeed, the larger dipole moments of 1,2,3,4-tetrachloro-6-phenylpentafulvene (II; R = H) in cyclohexane and benzene are almost identical (2·86 and 2·79 D).


(I)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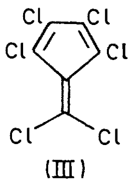
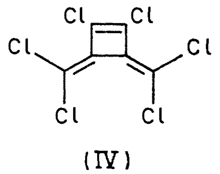

(III)


(IV)

Recently, Brown and his co-workers[13] determined by microwave spectroscopy the dipole moment of the parent hydrocarbon pentafulvene (in the gas phase), and found a value of 0·49 D.† Our considerably higher experimental value of 1·00 D ($\alpha' = 1\cdot66$, $\beta' = -2\cdot51$, $P_{2\infty} = 74\cdot0$ cm^3, MR$_{\text{calc}} = 53\cdot7$ cm^3) obtained for hexachloropentafulvene (III)[14] in cyclohexane solution seems to indicate, in contrast to the case of pentafulvene, a certain contribution of a

† This value is "startlingly different"[13] from the previous experimental values of *ca.* **1·1D, extrapolated from** solvent measurements on 6,6-disubstituted pentafulvenes; see P. Yates, *Adv. Alicyclic Chem.*, 1968, **2**, 59.

dipolar structure to the ground state of (III). The dipole moment of the isomeric 1,2-dichloro-3,4-bis(dichloromethylene)cyclobutene (IV)[15] in cyclohexane solution, 0·63 D [$\alpha' = 1{\cdot}33$, $\beta' = -2{\cdot}50$, $P_{2\infty} = 67{\cdot}6$ cm^3, $MR_{meas} = 59{\cdot}7$ cm^3; $\mu = 0{\cdot}82$ D from the calculated molar refraction (53·9 cm^3)] is significantly lower than that of (III), and practically identical with that of the parent hydrocarbon 3,4-dimethylenecyclobutene (0·62 D in the gas phase).[16] The concept of pseudoalternation[17,18] is thus applicable also to the series of cyclic conjugated perchlorocarbons.

The results reported here emphasize the need to consider the possibility of complex formation when determining dipole moments of chlorocarbon compounds in solution.

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