CONJUGATED CYCLIC CHLOROCARBONS: TRICHLOROCYCLOPROPENIUM ION, HEPTACHLOROTROPENIUM ION, AND OCTACHLOROFULVALENE

ROBERT WEST

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, USA

ABSTRACT
The properties of the aromatic trichlorocyclopropenium ion ($C_3Cl_3^+$) are described. Evidence from vibrational spectroscopy indicates that the C—C bonds in $C_3Cl_3^+$ are unusually short and strong. $C_3Cl_3^+$ undergoes Friedel–Crafts condensation reactions with aromatic hydrocarbons; with phenols, diarylquinocyclopropenes are obtained, which upon oxidation yield novel triquinocyclopropanes which show highly unusual electronic spectra. The seven-ring analogue to $C_3Cl_3^+$, heptachlorotropylium ion ($C_7Cl_7^+$), is obtained from octachlorobicyclo[3,2,0]heptane and aluminium chloride at 150° to 175°. $C_7Cl_7^+$ undergoes chemical reactions similar to those of $C_3Cl_3^+$. Water converts $C_7C_7^+Al_2Cl_7^-$ to octachlorocycloheptatriene, which upon solvolysis with sulphuric acid is transformed to perchlorotropone.

The compound octachlorofulvalene, $C_{10}Cl_8$, and its bromo analogue $C_{10}Br_8$ have been investigated. Both compounds show strong bathochromic shifts of electronic bands, due to twisting of the rings about the central double bond. $C_{10}Cl_8$ is a strongly electron-deficient molecule which serves as a powerful π-type charge-transfer acceptor toward aromatic hydrocarbons. The charge-transfer spectra are discussed.

The chemistry of the chlorocarbons—fully or highly chlorinated organic compounds—is now undergoing a renaissance, in which many of the most interesting findings centre about the cyclic conjugated perchloropolyenes. Monocyclic members of this family are shown in *Figure 1*. Of these species only hexachlorobenzene was known before 1964. Within the last six years the stable species $C_3Cl_3^+$, $C_7Cl_7^+$ and C_8Cl_8 have been isolated (the cations as salts) and the transient existence of C_4Cl_4, $C_5Cl_5^+$ and $C_5Cl_5^-$ has been convincingly demonstrated[1].

The family of species in *Figure 1*, like the cyclic polyenes from which they are derived, can be classified as aromatic if they contain $4n + 2$ and anti-aromatic if they contain $4n$ pi-electrons. Thus $C_3Cl_3^+$, $C_5Cl_5^-$, C_6Cl_6 and $C_7Cl_7^+$ can be considered aromatic and so are expected to be stabilized, but C_4Cl_4, $C_5Cl_5^+$ and C_8Cl_8 are antiaromatic and should be destabilized, at least when planar. However, the chlorine substituents may perturb the carbocyclic pi system either by withdrawing electronic charge inductively
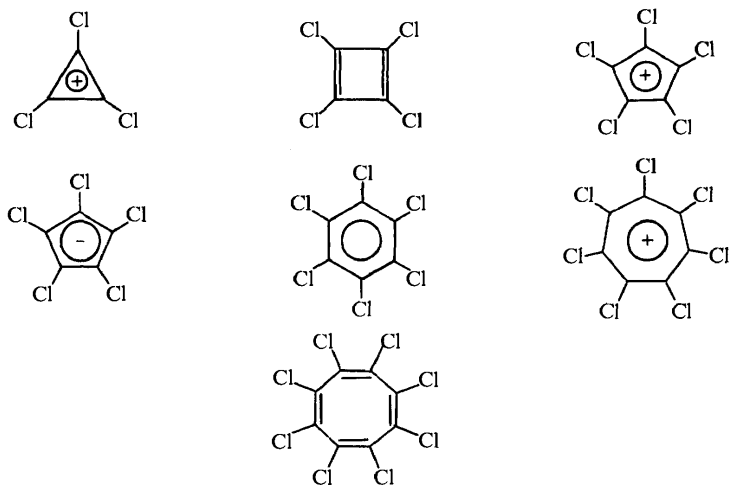
379

Figure 1. The monocyclic conjugated chlorocarbons.

through the C—Cl sigma bonds, or by direct participation of the non-bonding pairs on the chlorine in pi interaction with carbon. Fragmentary evidence suggests that both effects may be significant in certain delocalized chlorocarbons[1].

This paper will discuss the chemistry of two of these species, $C_3Cl_3^+$(I) and $C_7Cl_7^+$(II), both of which can be considered aromatic according to the usual rules. In addition, in the final section of the paper the chemistry of the interesting conjugated molecule octachlorofulvalene will be described.

I. TRICHLOROCYCLOPROPENIUM ION

This simple aromatic species was first synthesized[2] in 1964, by chloride abstraction from tetrachlorocyclopropene (III), with aluminium chloride or other powerful Lewis acid-halide acceptors:

$$C_3Cl_4 + MCl_3 \rightarrow C_3Cl_3^+, MCl_4^-$$

III $\qquad\qquad$ M = Al, Ga, Fe; also SbCl$_5$
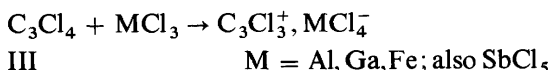
The starting material (III) is synthesized by dehydrohalogenation of pentachlorocyclopropane by warm concentrated aqueous potassium hydroxide solution in a two-phase system[3]. Pentachlorocyclopropane is obtained by addition of dichlorocarbene to trichloroethylene; but the latter olefin is rather unreactive toward carbene addition, so most methods for carrying out this reaction give only very small yields. However, when sodium trichloroacetate is thermolysed in dimethoxyethane at 80° in the presence of trichloroethylene, pentachlorocyclopropane is produced in 25 per cent yield[4].


380
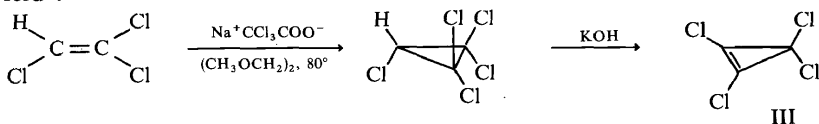
Tetrachlorocyclopropene prepared by this route is now available commercially in the USA. It shows promise as a vapour-phase fumigant as well as being useful as a chemical intermediate.

Substitution reactions on III normally take place with ring opening but with boron tribromide, III gives BCl_3 and tetrabromocyclopropene[3]. This reaction probably takes place through the formation of I as an intermediate and successive Br–Cl exchange reactions:
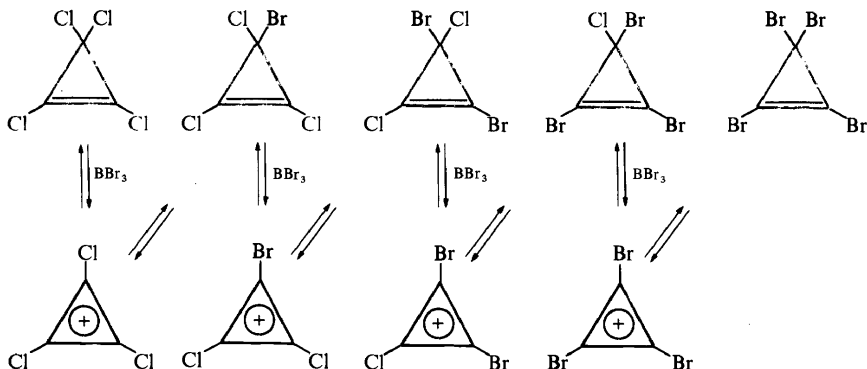
Partially fluorinated cyclopropenes can also be prepared from III, by treatment with SbF_3 in the presence[3] of $SbCl_5$, or with KF in tetramethylene sulphone[5]:
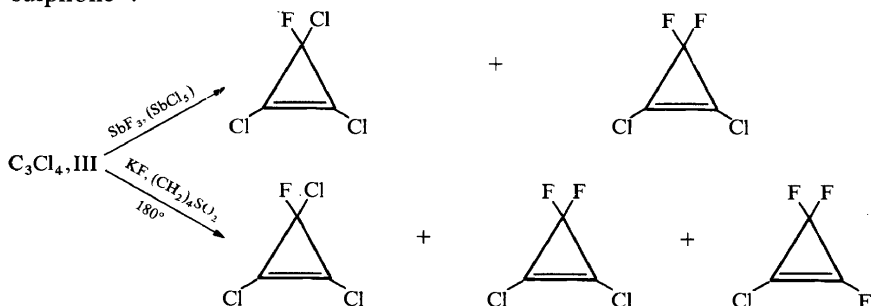
These halogenated cyclopropenes can all serve as precursors to trihalocyclopropenium ions, when treated with appropriate halide acceptors, i.e.:

$$C_3Br_4 \xrightarrow{\text{AlBr}_3} C_3Br_3^+, AlBr_4^-$$
$$C_3Cl_3F \xrightarrow{\text{AlCl}_3} C_3Cl_2F^+, AlCl_4^-$$
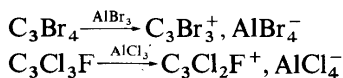
At the time it was prepared $C_3Cl_3^+$ was the simplest aromatic species known, having just six atoms and D_{3h} (triangular) symmetry[6]. The bonding in I was investigated using vibrational spectroscopy and normal coordinate analysis. Observation of the infra-red spectrum presented no difficulty, but to determine the Raman spectrum measurement in solution in liquid sulphur dioxide was required. The resulting Raman spectrum is shown in *Figure 2*. Observed frequencies are given in *Table 1*[7].

There are six constants in the Urey–Bradley force field used for the

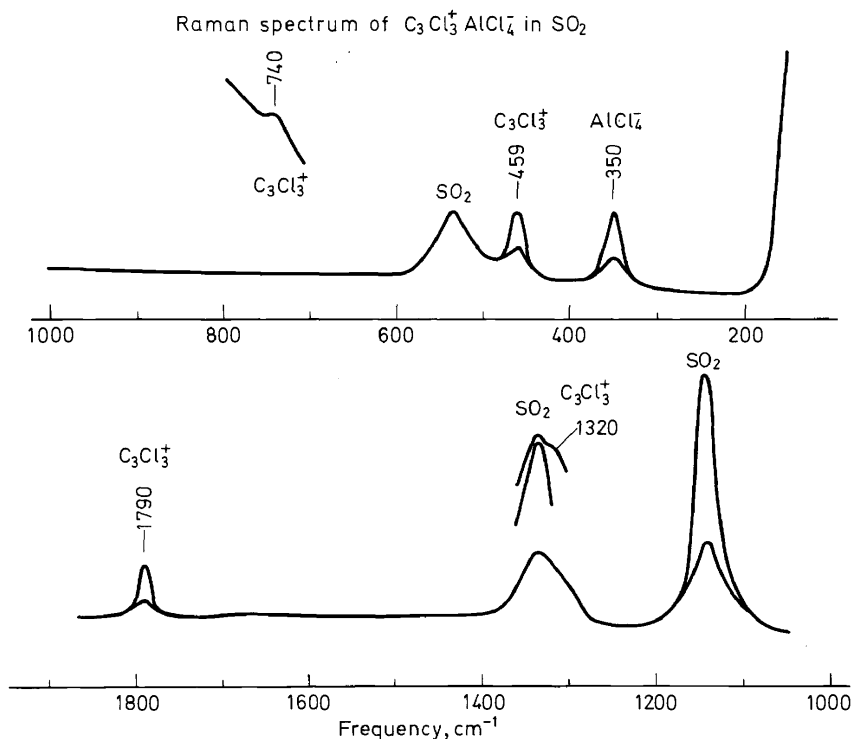Raman spectrum of $C_3Cl_3^+$ $AlCl_4^-$ in SO_2

Figure 2. Raman spectrum of $C_3Cl_3^+$ $AlCl_4^-$ in liquid sulphur dioxide, showing polarization.

calculation and only five fundamental frequencies were observed, so one constant must be assumed; but fortunately the chlorine atoms are so far apart that the nonbonded interaction constant can be taken as zero[7]. The results of a Urey–Bradley calculation are shown in *Table 2*, together with those from a partial normal coordinate analysis for the corresponding brominated ion, $C_3Br_3^+$. In *Table 3*, the C—C and C—Cl stretching force constants are compared with those for other known aromatic species. Note that both K_{CC} and K_{CCl} are decidedly higher than for chlorobenzene; indeed K_{CC} for $C_3Cl_3^+$ is *markedly higher than for any other known aromatic species.* Consistent with this is the x-ray finding by Sundaralingam, that the C—C distance in triphenylcyclopropenium ion is shorter than that in benzene[8].

Table 1. Vibrational frequencies for $C_3Cl_3^+$

cm^{-1}	Infra-red	Raman	Assignment
200	s	—	E
459	—	s, pol	A_1
735	s	vw	E
1312	vs	s, dep	E
1348	s	—	—
1791	—	m, pol	A

382

Table 2. Force constants for $C_3X_3^+$, millidynes/Å[7]

Species	$C_3Cl_3^+$	$C_3Br_3^+$
K_{CC}	6.31	6.46
K_{CX}	2.99	2.15
H_{CCC}	−0.248	(−0.248)*
H_{CCCl}	0.385	(0.275)
F_{CCl}	0.808	(0.674)
C_{ClCl}	(0)	(0)

* Values in parentheses are assumed.

Why should the C—C bond in cyclopropenium ions be so strong? Simple Hückel calculations predict a pi bond order of 0.667 for cyclopropenium, identical to that for benzene. The sigma bonding in cyclopropenium ions is probably external to the ring and 'bent' even more strongly than in cyclopropane or cyclopropene (*Figure 3*); if so the sigma bonds should be weaker

Table 3. C—C and C—Cl stretching force constants for aromatic species

Species	K_{CC}	K_{CX}	ρ
C_6H_6	5.59	4.67	0
	5.15	4.79	0.35
$C_5H_5^-$	5.39	4.79	0.21
C_6Cl_6	4.81	2.30	0.37
$C_3Cl_3^+$	6.32	2.99	0

ρ = Resonant constant.

than in benzene. But bending of the sigma bonds may bring the carbon atoms closer together, allowing for much increased overlap of p orbitals on adjacent carbon atoms. According to this model the unprecedented bond strength in $C_3Cl_3^+$ arises from the increased pi-bonding in cyclopropenium ions, which more than makes up for the decreased sigma bond strength.

In I, contributions from the chlorine atoms to the pi-bonding may also aid in raising both C—Cl and C—C bond strengths and force constants.
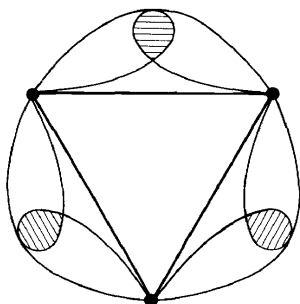

Figure 3. Schematic drawing of orbitals forming C—C bonds in cyclopropenium ions, indicating overlap external to the three-membered ring.

Nuclear quadrupole resonance measurements of Lucken and Mazeline[9] give a value of 0.35 for the asymmetry parameter η for the ^{35}Cl nuclei in I. This asymmetry parameter can be related directly to the partial double bond character, which is found to be 0.16. Both the asymmetry parameter and the bond order are higher than for any other known carbon–chlorine compound. The data suggest that about half of the positive charge on the ring (3×0.16) is delocalized through the pi system on to the chlorine atoms[9].

The chemistry of I has been reviewed elsewhere[1], so only those reactions which lead to compounds of some theoretical importance will be treated here. Hydrolysis of the tetrachloroaluminate salt of I, by flooding with water, leads to the regeneration of III in good yield[7]. Apparently water first attacks the $AlCl_4^-$ counterion rather than $C_3Cl_3^+$, forming chloride which converts I to C_3Cl_4. However, very slow solvolysis of I, preferably as the heptachlorodialuminate salt dissolved in dichloromethane, leads to the explosive liquid, dichlorocyclopropenone[10]. The reaction is best carried out using alcohol, and the first product is the $AlCl_3$ complex of the cyclopropenone. Further alcoholysis of the complex converts it to an alkoxychlorocyclopropenone[11], but the last chlorine atom is removed simultaneously with ring-opening. Upon **cautious** warming dichlorocyclopropenone is converted to a spirolactone:
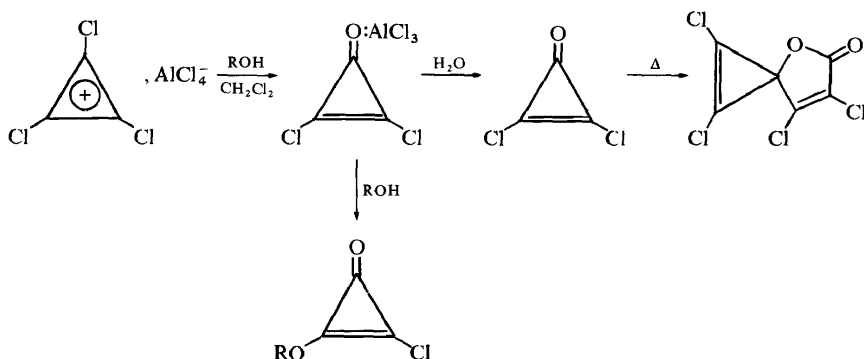

However, this reaction may take place with mild detonation above 0°, so *quantities of dichlorocyclopropenone greater than 1g should never be prepared.*

The trichlorocyclopropenium ion undergoes a useful and important Friedel–Crafts type reaction with aromatic hydrocarbons, leading to successive replacement of chlorine atoms with aryl groups to form arylhalo- and eventually triaryl-cyclopropenium ions. (The final step to give $Ar_3C_3^+$ requires, so far at least, an activated aromatic compound.) The arylated cyclopropenium ions give a variety of products on hydrolysis. Thus $ArC_3Cl_2^+$ yields the aryltrichlorocyclopropene or the arylhydroxycyclopropenone[12]. This is by far the most convenient synthesis of arylhydroxycyclopropenones, which are strong protonic acids. Hydrolysis of $Ar_2C_3Cl^+$ yields diarylcyclopropenones; the aryl groups can be the same or different, so this is a flexible and general method for synthesis[12].

384
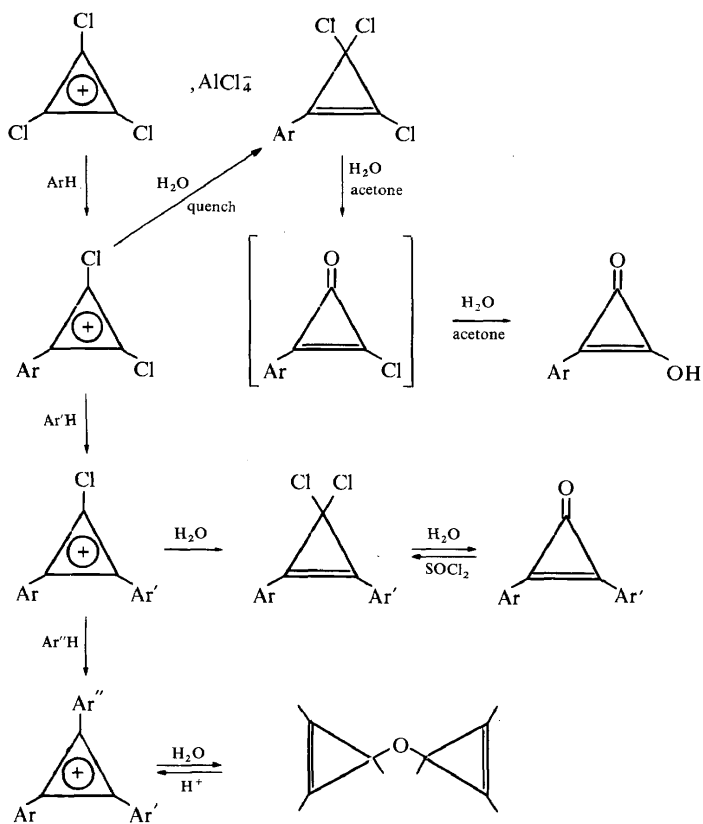
Especially interesting products are obtained when $C_3Cl_3^+$ is allowed to react with phenols. If a diarylchlorocyclopropenium ion, for instance, is treated with a phenol, the product is a p-hydroxyaryldiphenylcyclopropenium salt, as expected. The latter, however, contains a phenolic proton easily removed by treatment with mild base, forming an orange or yellow diaryl-quinocyclopropene[13].
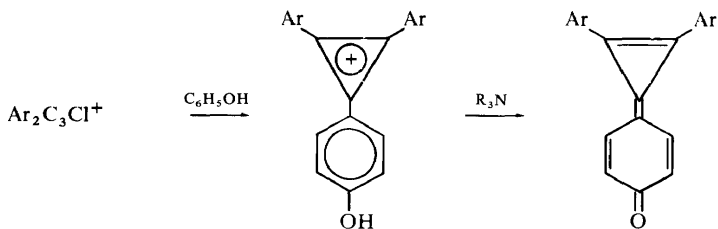
Diarylquinocyclopropenes are relatively little-known; at the time our work was carried out, only two examples were known, both obtained by more laborious syntheses[14, 15]. Starting from $C_3Cl_3^+$ it is now possible to prepare these substances quite conveniently.

385

If all three aromatic groups allowed to react with I are phenols (preferably 2,6-disubstituted), tris(p-hydroxyaryl)cyclopropenium ions are formed; these readily lose protons to form bis(hydroxyaryl)quinocyclopropenes. The latter undergo reversible oxidation to yield a remarkable new class of compounds, the triquinocyclopropanes (V)[13].
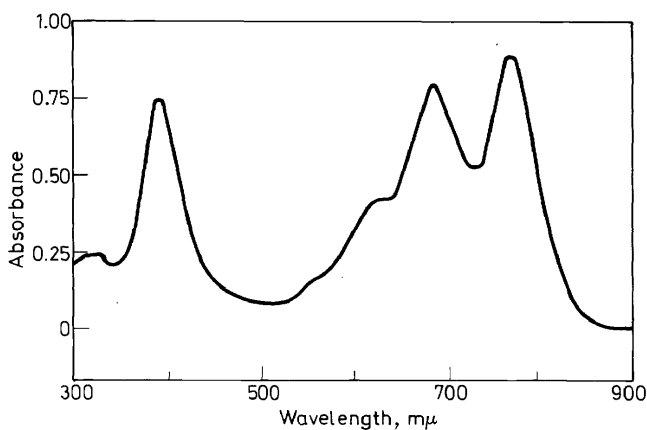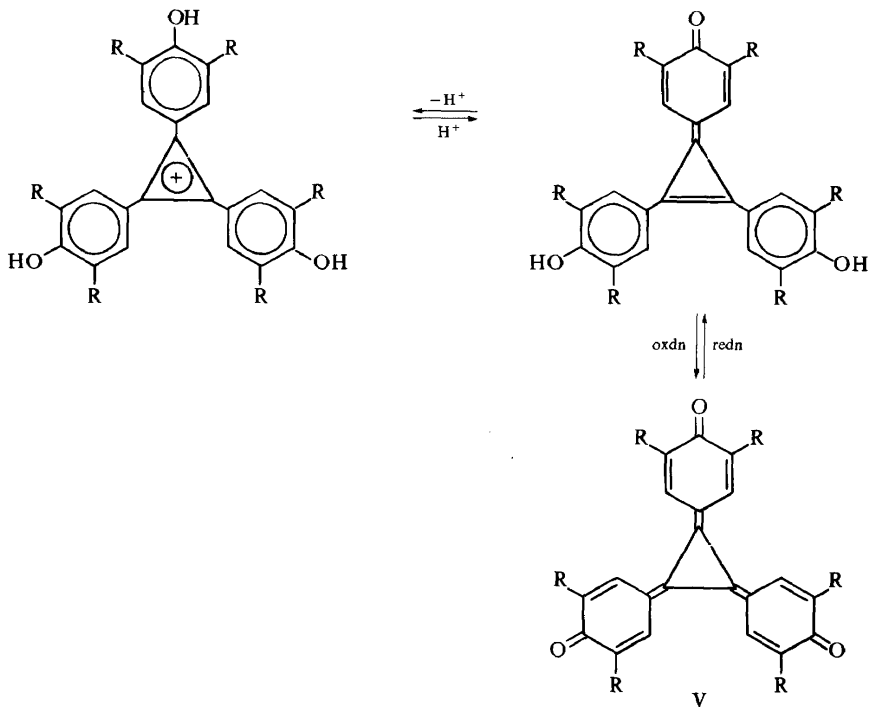

Figure 4. Electronic spectrum of hexa-*t*-butyl triquinocyclopropane (V, R = *t*-butyl) in dichloromethane.

The triquinocyclopropanes are intensely violet coloured substances, remarkable in that their electronic absorption spectra extend throughout the visible and into the near infra-red; the strongest bond occurs at about $\lambda = 770$ nm, with log $\varepsilon = 4.7$. The electronic spectrum of V, R $=$ *tert*-butyl, is shown in *Figure 4*. Compounds of this class are derivatives of 3-radialene, but are much more stable than normal 3-radialenes; some triquinocyclopropanes will withstand heating to over 200°. The anion-radical and dianion corresponding to V have also been prepared[16]. The e.s.r. spectrum of the anion-radical shows a symmetrical 7-line pattern (*Figure 5*) consistent with complete delocalization of the unpaired electron over the four-ring system.


10 e
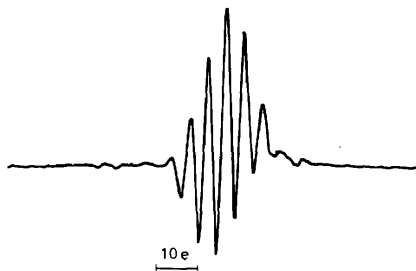
Figure 5. Electron spin resonance spectrum of anion radical of V (R $=$ *t*-butyl).

Both neutral triquinocyclopropanes and their dianions have singlet ground states, in agreement with simple molecular orbital calculations.

II. HEPTACHLOROTROPYLIUM ION

Tropylium ion, $C_7H_7^+$, is well known as a stable, six-π-electron cation. Following isolation of $C_3Cl_3^+$, attention was turned to synthesis of the seven-membered ring analogue, $C_7Cl_7^+$. Starting material for this synthesis was the bicyclic compound made from hexachlorocyclopentadiene, trichloroethylene, and aluminium chloride[17]. Dehydrohalogenation leads to octachlorobicyclo[3,2,0]heptadiene (VI), which reacts with aluminium


VI
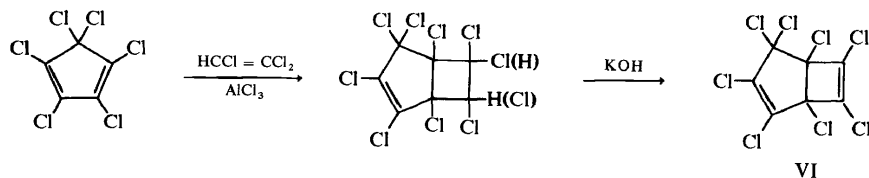
chloride on warming. Below 150° the bicyclic compound is regenerated on hydrolysis, and above 180° complete fragmentation occurs, but in the intermediate 30 deg. temperature range isomerization takes place to heptachlorocycloheptatrienium heptachlorodialuminate, which hydrolyses to octachlorocycloheptatriene (VII)[18]. This is a colourless crystalline compound, m.pt 86°, which reacts with $AlCl_3$ to form the yellowish tetrachloroaluminate salt of II. Similar 1:1 salts are formed between VII and $SbCl_5$,

387

$SnCl_4$ or $FeCl_3$. The salts of II have essentially identical infra-red spectra above 600 cm^{-1}, consisting of just four bands at 1 252(w), 1 180(s), 750(w) and 700(s), in cm^{-1}. At lower frequencies, bands characteristic of the halometallate ions are observed (*Figure 6*). All of these salts regenerate VII upon treatment with water.
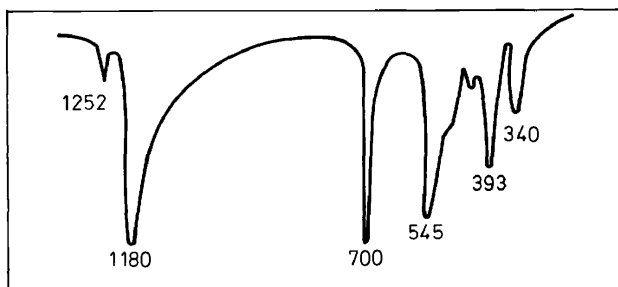

Figure 6. Infra-red spectrum of $C_7Cl_7^+ Al_2Cl_7^-$, as mull in petroleum oil.

Models indicate that lone pairs on adjacent chlorine atoms would inter-fere strongly in the ion II if it were planar. The geometry of II is unknown, but it seems to have much of the aromatic character of tropylium ions generally. It is at least as stable with respect to VII and Lewis acids as $C_3Cl_3^+$ is with respect to its parent chlorocarbon C_3Cl_4. The chemical reactions of
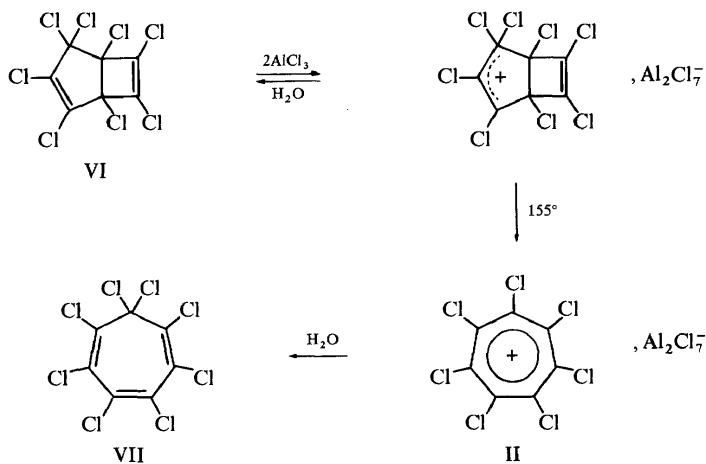

II are as yet little known, but appear to resemble those of $C_3Cl_3^+$. For example, II reacts with aromatic hydrocarbons to give Friedel–Crafts sub-stitution. With phenols, loss of a proton takes place to yield quinotropones. It seems probable that $C_7Cl_7^+$ will prove a valuable intermediate in the synthesis of other novel delocalized structures, just at $C_3Cl_3^+$ is.
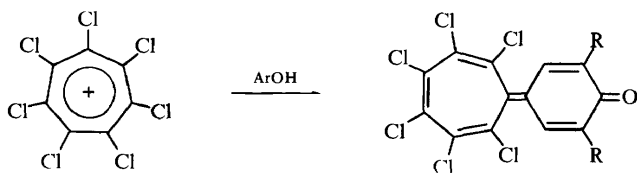
Halogen exchange reactions of VII also take place, probably through the intermediate formation of II[19]. When VII is warmed with boron tribromide, *seven* of the eight chlorine atoms are replaced by bromine, giving C_7Br_7Cl (VIII). The remaining chlorine probably is in the geminal position and resists replacement for steric reasons. Solvolysis of VII with concentrated sulphuric acid yields perchlorotropone, which has also been synthesized by an independent photochemical method. Similarly, sulphuric acid treatment of VIII yields perbromotropone, which can also be made[19] from perchlorotropone and BBr_3 :
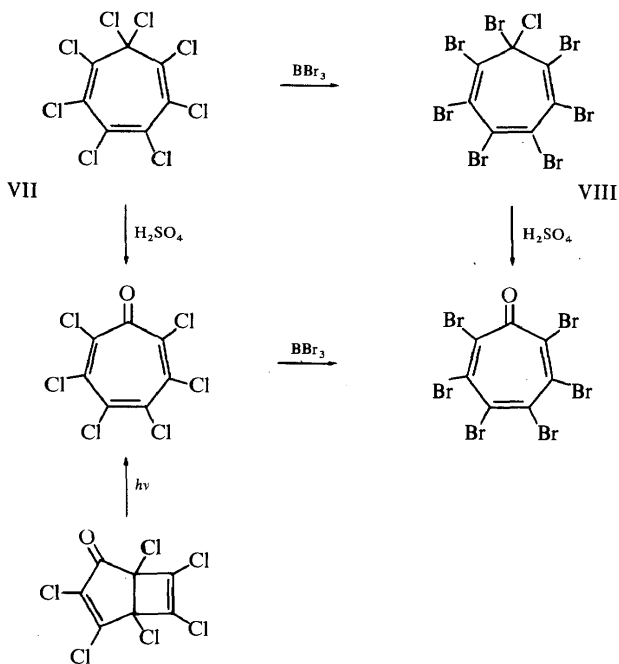
### III. Octachlorofulvalene(X) and Its Charge-Transfer Properties

This fascinating chlorocarbon was first prepared by V. Mark[20] via dehalogenation of decachlorobi(2,4-cyclopentadien-1-yl), IX, which can be synthesized from hexachlorocyclopentadiene and copper or copper(I) chloride. Mark used triethyl phosphite in the final step, but a slightly better yield can be obtained with stannous chloride dihydrate in acetone[21] :

389
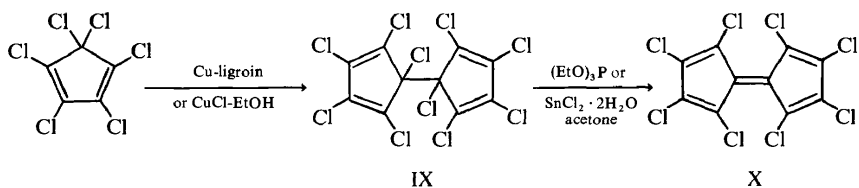
X has also been obtained by gas-phase dechlorination of hexachlorocyclo-pentadiene at high temperature[22]. Compared with other fulvalenes, X is remarkably inert and quite different in physical and chemical properties. Fulvalene itself is an orange-coloured material so unstable that it cannot be isolated, but X is easily obtained as beautiful blue-violet crystals.

The chlorination of X has recently been investigated, and the several products have been isolated and identified with the aid of nuclear quadrupole resonance spectroscopy[21]:
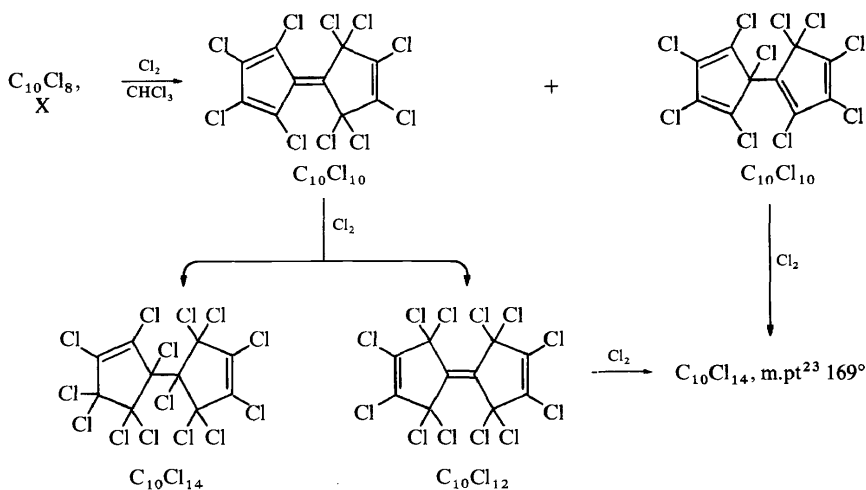
The perbromo analogue, octabromofulvalene (XI), has also been syn-thesized, directly from hexabromocyclopentadiene[24].
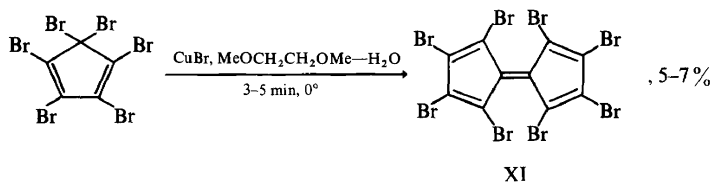
The perbromo compound XI is less stable thermally and more reactive chemically than X, but the two compounds show quite similar spectral properties. The electronic spectra of these substances are shown in *Figure 7*. Both compounds show a strong band near 400 nm, and a broad band

390

between 600 and 650 nm. In contrast, fulvalene itself and simple substituted fulvalenes show their longest wavelength absorption near 415 nm.

The striking bathochromic shift for X and XI compared to ordinary fulvalenes may reflect in part contributions from nonbonded electrons on halogen, but are probably due principally to twisting of the central C—C double bond joining the rings. A two-dimensional x-ray study of X has indicated a dihedral angle of 41° between the two rings[25], which are twisted out of the preferred planar configuration by steric repulsions of the chlorine atoms at the 2, 2′, 5 and 5′ positions. Nonplanarity of the fulvalene rings has
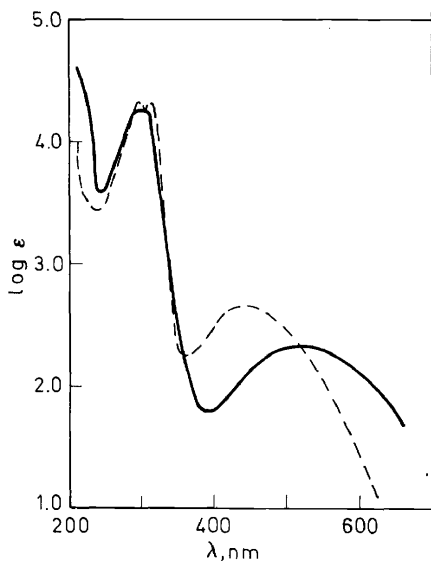

Figure 7. Electronic spectra of octahalofulvalenes in dichloromethane solution. ————, $C_{10}Cl_8(X)$; – – – – –, $C_{10}Br_8(XI)$.

previously been associated with bathochromic shifts of electronic transitions in fused-ring fulvalenes[26]. The molecular structure of XI is not yet known, but the steric interactions should be even greater than in X, so the inter-ring angle will be of considerable interest.

Fulvalenes generally are electron-deficient molecules possessing an unfilled pi-orbital, and in octachlorofulvalene, according to HMO calculations, this orbital is at even lower energy than in fulvalene itself (*Figure 8*)[27]. Consistent with this is the finding that X forms charge-transfer complexes, acting as a pi-acid. This property allows a spectacular demonstration of colour changes upon charge-transfer complex formation. Solutions of X in noninteracting solvents such as dichloromethane are blue. Addition of benzene or toluene changes the colour to green; mesitylene gives a yellow colour; phenanthrene, a yellow-brown; and with pyridines, red!

Spectral changes upon charge-transfer complex formation with X are subtle. The electronic spectrum of X contains bands at 390 nm (log ε = 4.60) and 604 nm (log ε = 2.40). In the presence of moderate pi-donors such as benzene

and toluene, these bands are unchanged except for some broadening and detensification of the shorter wavelength band (*Figure 9*). In mesitylene, however, the 390 nm band of X is significantly broadened on its longer wavelength side. Such one-sided broadening must be due to the presence of a new band in the 400–475 nm region of the spectrum (illustrated in *Figure 9*). A set of similar curves is obtained when the spectra of X are plotted as one increases the concentration of an aromatic compound (*Figure 10*). In both of these cases the concurrent broadening of the 390 nm band of X and 'filling in' of the absorption minimum near 475 nm shifts the $\lambda_{min.}$ to longer wavelengths and so gives rise to the observed colour changes[27].
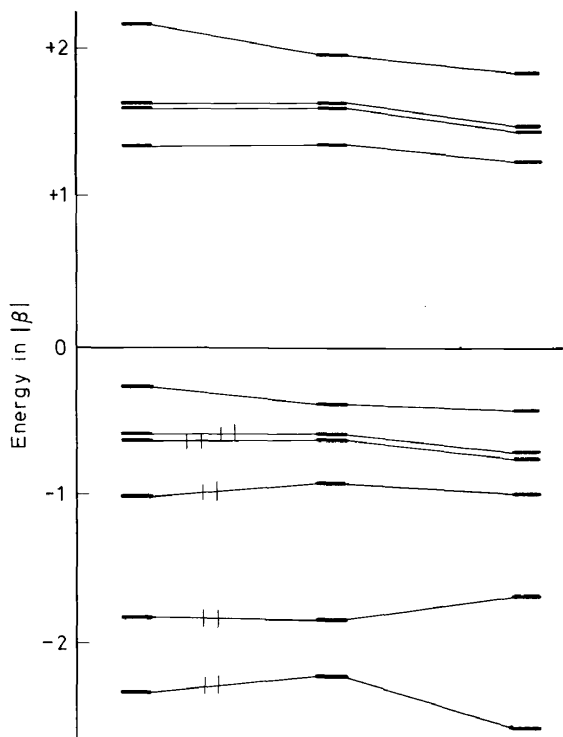
Figure 8. Schematic representation of the π molecular orbitals for fulvalene (left), twisted fulvalene (centre), and octachlorofulvalene(X) (right).

The spectral absorption in the 475 nm region was studied as a semi-quantitative measure of the effects of various donors on the spectra of X. Δ Log ε (at 475 nm, relative to cyclohexane) was measured as a function of donor/acceptor mole ratio for a large number of donors. The results of this study are summarized in *Table 4* and *Figure 11*. In non-aromatic solvents, including dioxane and acetone, the spectrum of X gives no indication of strong charge-transfer complex formation. The slight spectral changes which are observed with dioxane probably arise from solvent shifts or *n*-donor charge-transfer. On the other hand, π-donors give rise to large values of Δ log ε,
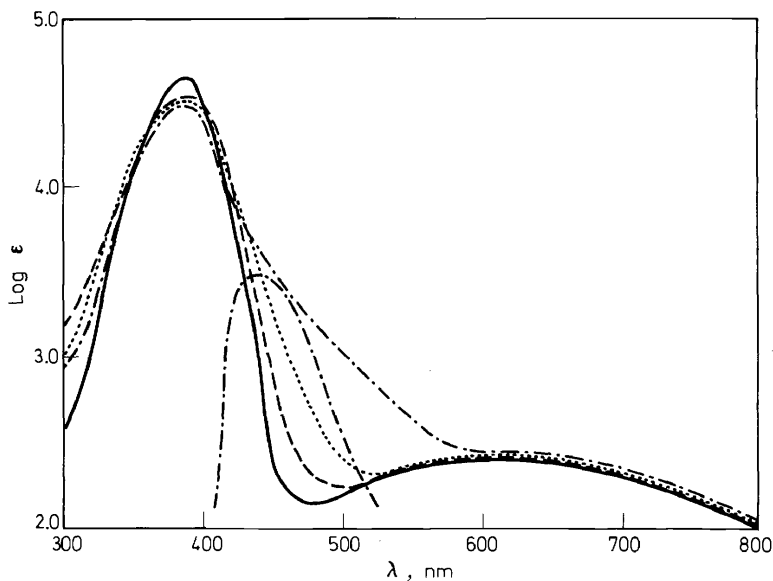
392

Figure 9. Variation in the electronic spectrum of $C_{10}Cl_8(X)$ with solvent; ——— methylene chloride; – – – benzene; ...... toluene; – · – · – · mesitylene. The position of the new band appearing in the presence of excess mesitylene, and attributed to the charge-transfer absorption, is also shown.
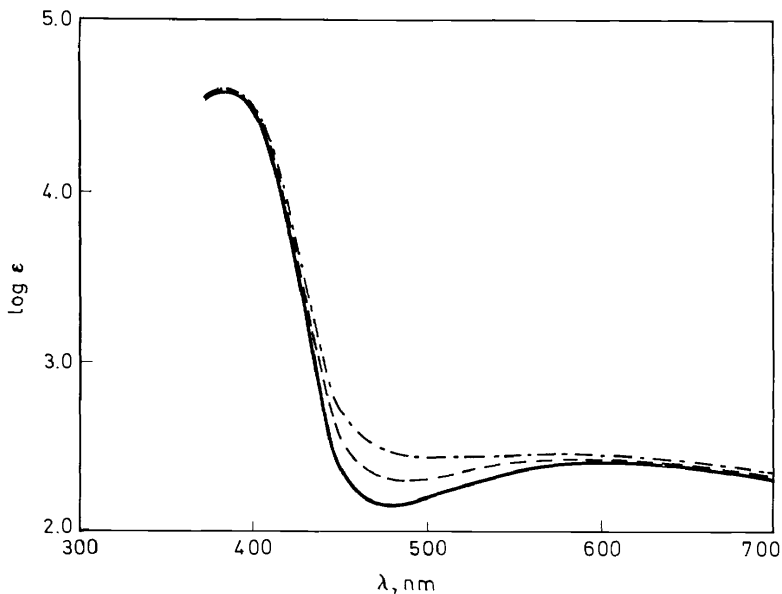

Figure 10. Variations in the electronic spectrum of octachlorofulvalene with increasing donor concentration. ($C_{10}Cl_8$/phenanthrene in CH_2Cl_2; mole ratio: 61 ———, 279 – – – –, 552 – . – .).

393

indicating the formation of strong molecular complexes. The data suggest the following sequences of donor potency:

pentamethylbenzene, durene > hexamethylbenzene, mesitylene > xylene > toluene > t-butylbenzene > benzene, chlorobenzene

and

benzopyrene > phenanthrene > pyrene > naphthalene > acenaphthene.

In general this is the same order of donor strength which is observed in other charge-transfer complex formation[28, 29]. Hexamethylbenzene and acenaphthene are less effective donors than expected, probably because of steric hindrance to complexation.
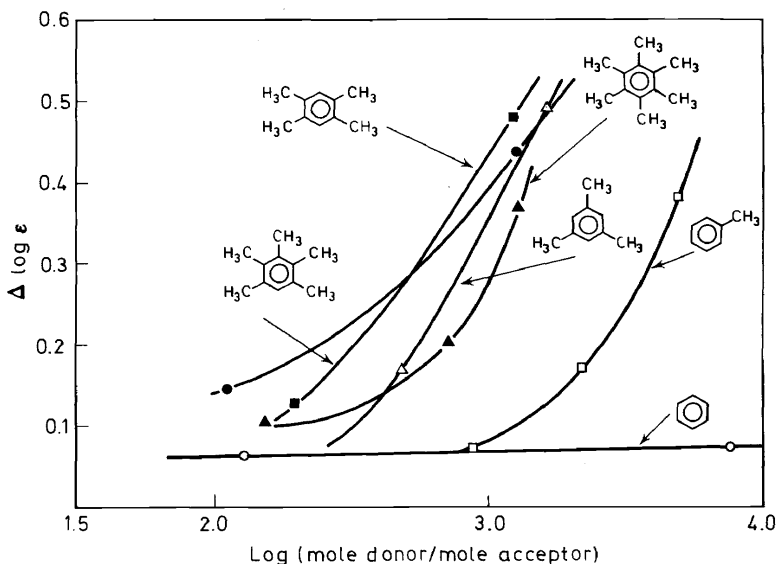

Figure 11. Charge-transfer complexes of octachlorofulvalene. Variation in log ε (at 475 nm) with mole ratio of donor to acceptor, for monocyclic aromatic donors.

Theoretically, increasing the concentration of a donor compound in a dichloromethane solution should lead to gradual changes in the spectrum of X until essentially all of the $C_{10}Cl_8$ is converted to the charge-transfer complex; beyond this point no further spectral changes should occur. The data in *Figure 11* show that no such levelling off of the Δ log ε versus mole ratio curves is observed below donor/acceptor ratios of 10^3 and apparently does not occur significantly even at mole ratios of 10^4. This observation leads to the conclusion that the equilibrium constants for charge-transfer complex formation,

$$K_{CT} = (C_{10}Cl_8 \cdot donor)/(C_{10}Cl_8)(donor)$$

cannot be greater than 10^{-3}. These values of K_{CT} are approximately three orders of magnitude smaller than those commonly observed in charge-transfer complex formation (for example, for the very stable tetracyano-ethylene–mesitylene complex $K_{CT} = 17.3$, and the relatively unstable iodine–benzene complex has $K_{CT} = 1.5 \times 10^{-1}$)[30].

Table 4. Effects of π-donors on the electronic spectrum of octachlorofulvalene

Donor	Mole ratio[a]	log ε (475 nm)	Δ log ε (475 nm)
Cyclohexane[b]	8.37×10^3	2.03	0.00
CH_2Cl_2[b]	2.79×10^4	2.10	+0.07
$CHCl_3$[b]	1.12×10^4	2.05	+0.02
CCl_4[b]	1.11×10^4	2.03	0.00
1,4-Dioxane[b]	2.28×10^4	2.16	+0.13
Ph—CF_3[b]	1.21×10^4	2.31	+0.28
Ph—H[b]	9.60×10^3	2.32	+0.29
Ph—Cl[b]	1.08×10^4	2.31	+0.28
Ph—CH_3[b]	9.04×10^3	2.84	+0.81
Ph—$C(CH_3)_3$[b]	6.46×10^3	2.64	+0.61
CH_3—C_6H_4—CH_3[b]	7.6×10^3	3.09	+1.06
Mesitylene[b]	6.29×10^3	3.31	+1.28
p-$C_6H_4(OCH_3)_2$[c]	2.12×10^2	2.11	+0.08
p-$C_6H_4(OCH_3)_2$[c]	5.99×10^2	2.18	+0.15
p-$C_8H_4(OCH_3)_2$[c]	1.75×10^3	2.29	+0.26
1,3,5-$C_6H_3(OCH_3)_3$[c]	6.65×10^2	2.34	+0.31
Acridine[c]	5.72×10^1	2.08	+0.05
Acridine[c]	3.84×10^2	2.30	+0.27

[a] Donor/acceptor.
[b] Donor used as the solvent.
[c] Spectrum run as solution in dichloromethane.

Although a large number of pi-donors were employed with X, in no case was it possible to observe the charge-transfer absorption band directly. With weak donors such as benzene and toluene this band apparently falls almost directly beneath the intense 390 nm band of X. With better donors (such as benzopyrene) absorption by the donor molecule (which must be present in large excess because of the low K_{CT}) further obscures observation of the charge-transfer band. However, for moderately strong pi-donors the charge-transfer band must lie between 400 and 475 nm, and this allows a rough comparison of the acceptor strength of X with that of other pi-acids. Data for a number of acceptors with various donors are given in Table 5. From this table it appears that X is a slightly more powerful acceptor than p-benzoquinone, and is comparable in pi-acid strength to chloranil or 1,2,3-indanetrione[27].

Although X is a relatively good pi-acceptor, it is not so strong as might be predicted from MO calculations. The energy of the charge-transfer transition, E_{CT}, is commonly given[34] as

$$E_{CT} = IP - EA + C$$

where IP is the ionization potential of the donor, EA is the electron affinity of the acceptor, and C is a constant denoting all other forms of energy

(solvation, etc.) changing upon complex formation. The electron affinity of X (LUMO at -0.4β, see *Figure 8*) should, from MO theory, be even greater than for tetracyanoethylene (LUMO -0.34β)[29]. The reason why X is a poorer pi-acid than TCNE probably lies in the C term and reflects the nonplanarity of X which prevents close approach of the pi-system of the donor. The fact that the equilibrium constants for charge-transfer complex formation to X are two or three orders of magnitude smaller than typically found for such complexes is consistent with this explanation. Thus octachlorofulvalene is a unique example of a *powerful but strongly sterically hindered pi-acid*[27].

Table 5. Charge-transfer absorption maxima for various complexes, nm

Substance	Benzene	Mesitylene	Naphthalene	Phenanthrene	Pyrene	Ref.
Tetracyanoethylene	385	—	560	540	720	31
Chloranil	339	427	390, 480	473	435, 599	32
1,2,3-Indanetrione	—	—	—	400	481	29
X	~350	400–475	400–475	400–475	—	27
p-Benzoquinone	284	344	367	—	448	32
Maleic anhydride	—	—	325	354	384	33

Although the twisted molecular form of X apparently limits its effectiveness as a charge-transfer acceptor, the geometry of X should favour its outright reduction to an anion radical or dianion. Imamura and Hoffmann have pointed out[35] that while fulvalene and its derivatives should prefer a planar ground state, the fulvalene dianion (isoelectronic with biphenylene) should prefer a nonplanar ground state. Hence the nonplanarity of X should add a driving force to the ability of X to accept electrons in the ground state.

Treatment of octachlorofulvalene with Na–K alloy in tetrahydrofuran at room temperature in an e.s.r. tube gave rise to a purple solution showing a single, rather sharp e.s.r. signal ($\Delta w_{\frac{1}{2}} = 2.4$ G; *Figure 12*a) at $g = 2.0048 \pm 0.0002$. The intensity of this signal slowly decreased with time, and within a few hours the signal disappeared entirely. Electrolysis of a solution of X in tetrahydrofuran with added tetra-*n*-butylammonium perchlorate at room temperature or at $-50°$ and with 1–2 µA current led to a similar purple solution and to the appearance of a similar e.s.r. signal ($\Delta w_{\frac{1}{2}} = 2.5$ G; *Figure 12*b) at $g = 2.0043 \pm 0.0001$. Continued electrolysis of this sample at somewhat higher currents (5–8 µA) caused the signal to decay slowly until it finally disappeared after about an hour. Numerous attempts to regenerate the radical species by reversing the leads to the electrolysis cell were unsuccessful.

The radical observed in both of these experiments is believed to be the anion radical of X. Both of these species were generated under 'minimal' reaction conditions (short contact times and low currents), and the species obtained by alkali metal reduction is remarkably stable even at room temperature ($t_{\frac{1}{2}} \sim 1$ h). The species obtained by electrolysis disappears easily upon further reduction, presumably to give the dianion of X. Reductions of both X and its anion radical are apparently irreversible, however; both the

anion radical and dianion of X decompose to nonradical products when attempts are made to oxidize these species[27].

Finally treatment of X with extremely powerful pi-donors appears to lead to ground-state charge-transfer, effecting oxidation of the donor and reduction of X. Two donors of this class have been studied; 2,6-lutidine
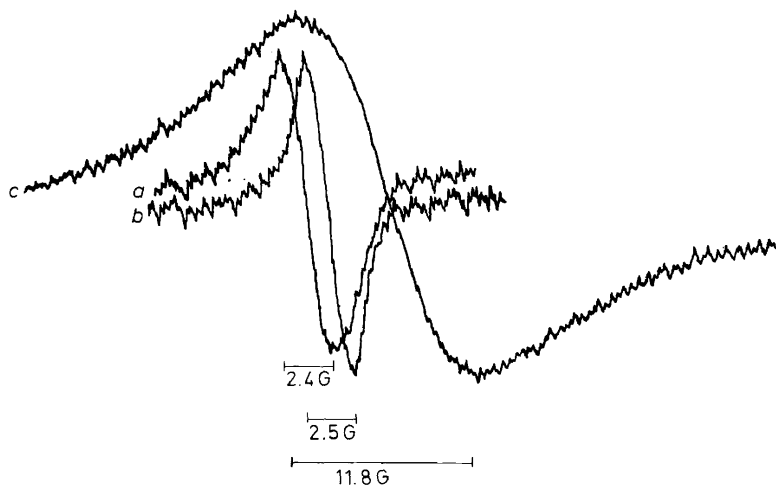

2.4 G

2.5 G

11.8 G

Figure 12. Electron spin resonance spectra, *a*, reduction product from octachlorofulvalene with sodium–potassium alloy in tetrahydrofuran; *b*, electrolytic reduction product of octachlorofulvalene in tetrahydrofuran; *c*, reaction product of octachlorofulvalene and *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine.

and *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD)[27]. When 2,6-lutidine is mixed with X in dichloromethane solution an e.s.r. spectrum for the cation radical of the amine is observed, but no signal due to the octachlorofulvalene. With TMPD, X gives a strong, broad e.s.r. line (*Figure 12*c) which may be characteristic for the ion-pair between TMPD cation-radical and the anion-radical of X. Further research on charge-transfer properties of X and related molecules seems most desirable.

REFERENCES

[1] R. West, *Accounts Chem. Res.* **3**, 130 (1970).
[2] S. W. Tobey and R. West, *J. Am. Chem. Soc.* **86**, 1459 (1964).
[3] S. W. Tobey and R. West, *J. Am. Chem. Soc.* **88**, 2481 (1966).
[4] S. W. Tobey and R. West, *J. Am. Chem. Soc.* **88**, 2478 (1966).

[5] D. C. F. Law and R. West, unpublished studies.
[6] More recently the cyclopropenium ion itself has been prepared: R. Breslow, J. T. Groves and G. Ryan, *J. Am. Chem. Soc.* **89**, 5048 (1967).
[7] R. West, A. Sadô and S. W. Tobey, *J. Am. Chem. Soc.* **88**, 2488 (1966).
[8] The C—C bond length in the three-membered ring in triphenylcyclopropenium perchlorate is 1.373 Å, compared to 1.39 Å for benzene. See M. Sundaralingam and L. H. Jenson, *J. Am. Chem. Soc.* **88**, 198 (1966).
[9] E. A. C. Lucken and C. Mazeline, *J. Chem. Soc. A*, 153 (1968).
[10] R. West, J. Chickos and E. Osawa, *J. Am. Chem. Soc.* **90**, 3885 (1968).
[11] J. Chickos and R. West, unpublished studies.
[12] R. West, D. C. Zecher and S. W. Tobey, *J. Am. Chem. Soc.* **92**, 168 (1970).
[13] R. West and D. C. Zecher, *J. Am. Chem. Soc.* **92**, 155 (1970).
[14] A. S. Kende, *J. Am. Chem. Soc.* **85**, 1882 (1963).
[15] B. Föhlisch and P. Bürgle, *Tetrahedron Letters*, 2661 (1965); *Ann. Chem.* **701**, 67 (1967).
[16] R. West and D. C. Zecher, *J. Am. Chem. Soc.* **92**, 161 (1970).
[17] A. Roedig and L. Hörning, *Ann. Chem.* **598**, 208 (1956), and references cited therein.
[18] R. West and K. Kusuda, *J. Am. Chem. Soc.* **90**, 7354 (1968).
[19] K. Kusuda, R. West and V. N. M. Rao, *J. Am. Chem. Soc.* **93**, 3627 (1971).
[20] V. Mark, *Tetrahedron Letters*, 333 (1961).
[21] R. M. Smith and R. West, *J. Org. Chem.* **35**, 2681 (1970).
[22] A. E. Ginsberg, R. Paatz and F. Korte, *Tetrahedron Letters*, 779 (1962).
[23] E. T. McBee, J. D. Idol Jr and C. W. Roberts, *U.S. Pat. No. 2911448* (3 November 1959); *Chem. Abstr.* **54**, 4527 (1960).
[24] R. West and P. T. Kwitowski, *J. Am. Chem. Soc.* **90**, 4697 (1968).
[25] P. J. Wheatley, *J. Chem. Soc.* 4936 (1961).
[26] E. D. Bergman, G. Berthier, A. Pullman and M. B. Pullman, *Bull. Soc. Chim. Fr.* 1079 (1950).
[27] R. M. Smith, *Ph.D. thesis*, University of Wisconsin (1970).
[28] L. J. Andrews and R. M. Keefer, *Molecular Complexes in Organic Chemistry*, p 21. Holden-Day: San Francisco (1964).
[29] A. R. Lepley and J. P. Thelman, *Tetrahedron*, **22**, 101 (1966).
[30] L. J. Andrews and R. M. Keefer, *loc. cit.* p 28.
[31] M. J. S. Dewar and H. Rogers, *J. Am. Chem. Soc.* **84**, 395 (1962).
[32] A. Kuboyama, *Nippon Kagaku Zasshi*, **81**, 558 (1960).
[33] M. Chowdhury, *J. Phys. Chem.* **66**, 353 (1962).
[34] H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.* **21**, 66 (1953).
[35] A. Imamura and R. Hoffmann, *J. Am. Chem. Soc.* **90**, 5379 (1968).