Alkylidenecycloproparenes: strained and polar aromatics

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Abstract - The alkylidenecycloproparenes are strained (~281 kJmol\(^{-1}\)) and polar (\(\mu\ 0.5\text{-}3.0\) D) compounds; the magnitude and direction of the permanent dipole depends upon the substitution pattern present. The dimethylaminophenyl derivative 17 fluoresces strongly (\(Y_\sigma 0.96\)). Flash vacuum pyrolysis of 12 and 19 leads to polycyclic aromatics by way of three-membered ring cleavage and insertion. Metal atom insertion and ring expansion occurs upon reaction with rhodium and platinum complexes.

The discovery that diarylmethylenecycloproparenes, cf. 1, are surprisingly stable coloured crystalline solids is recent and is in marked contrast to their 1-oxo analogues, the benzocyclopropenones (refs. 1-3). Stable derivatives of methylenecyclopropene have been known for twenty-five years (ref. 4) but the parent hydrocarbon has only recently been reported (ref. 5) and is unstable at temperatures above -75°C. Similarly, the smallest parent radiale, trimethylenecyclopropane, polymerizes above 0°C (ref. 6). The alkylidenecycloproparenes, eq. 1, combine into one molecule the features associated with both of these hydrocarbons. Thus they may be regarded as a cycloproparene 1a, a benzannulated methylenecyclopropene 1b, a benzannulated triafulvene 1f, an unusual radiale 1d, and an inversely polarized fulvene 1e-1f all in one.

The most general route to the alkylidenecycloproparenes couples the acidity of the benzylic protons of the parent cycloproparene hydrocarbon with Peterson olefination (Scheme 1) and with suitable modification the sequence is applicable to the preparation of the corresponding cyclopropa[2]napthalene homologues (refs. 2,3). Because base is necessary for carbanion formation, carbonyl compounds which carry an \(\alpha\)-hydrogen frequently fail to react presumably

\[ \text{Scheme 1} \]
because of enolate ion formation. Furthermore the methodology has yet to yield parent species, eg. 1. The widest application of the route is to derivatives which carry aryl- or diarylmethylene substitution and a good range of such compounds as stable, colored crystalline solids now exists (refs. 2,3,7,8).

Apart from these fulvenes the fluorenylidene 5 and dibenzocycloheptatrienylidene 6 derivatives are available (ref. 7). The compounds have measurable permanent dipole moments (5: 2.6 D; 6: 1.2 D) which are in excellent agreement with the values calculated for the parent systems 7 (3.28 D) and 8 (1.12 D) respectively (ref. 9). Especially noteworthy is the fact that the direction of the calculated dipole in 1, 7 and 8 is the same. It follows, therefore, that the cycloheptatrienyl moiety is not a strong enough electron donor to reverse the polarity to a 6n7C tropylium cation/benzylic anion contributor, cf. 1e-f. The same direction of polarity (viz. 1e) is presumed to be present in the dibenzo homologue 8 and is supported by the outcome of electrophilic additions which effect protonation at Cl', the negative end of the dipole, to deliver (ultimately) ring cleaved and ring expanded products (Scheme 2).

The preparation of alkylidenecyclopropa[n]benzenes with effective electron donating substituents attached to the exocyclic double bond has now been accomplished and the compounds have significant permanent dipoles (Chart 1). Notable amongst these compounds is the dinitro derivative 15. Because of the sensitivity of 4,4'-dinitrobenzophenone to t-butoxide the preparation of 15 from disilylcyclopropa[b]naphthalene (ref. 2) requires a modified procedure. The reaction is effected in acetonitrile by employing an excess of insoluble potassium fluoride. The anion is transferred by a catalytic quantity (25 mol %) of tetrabutylammonium fluoride and dinitro 15 is obtained in 88% yield; the reaction fails for the cyclopropabenzene equivalent. Unfortunately compound 15, which clearly

Scheme 2

\[ R = H \quad \mu = 2.6 \text{ D} \quad R = H \quad \mu = 1.2 \text{ D} \]
should have polarity in the opposite direction to that in 14, is insufficiently soluble in benzene to allow for capacitance measurements and dipole moment calculation. However the polar natures of e.g. 5 and 11 establish that the cyclopropene moiety is ambiphilic (ref. 8). The charge separation, \( \epsilon_{le-f} \), is dictated therefore by the nature of the substituents attached to the exocyclic double bond. The polarity of the compounds is reflected in the intensity of the characteristic (ref. 3) infrared stretching vibration at \( \sim 1770 \text{ cm}^{-1} \) (Fig. 1). This band results from a combination of the three-membered ring endo- and exocyclic double bond stretches; as the polarity increases the intensity decreases. Notable is the fact that removal of the non-bonding electron pairs by quaternization of the nitrogen atoms of 11 (14 or 15) restores the combination band. A similar effect occurs for the long wavelength ultraviolet absorption maxima (ref. 8).

During the isolation of the dimethylamino substituted compounds, and especially 17, it became obvious that the extended conjugation and the nature of the substituents provided a notable lumophore. Emission spectroscopy has established that compounds 10, 11, 13, 14, 16 and 17 are markedly more fluorescent than their parents. The absolute quantum yields (\( \Phi_F \)) for 14 and 17 in cyclohexane are 0.81 and 0.96 respectively (refs. 10,11). Fig. 2 depicts the absorption-emission characteristics of 17 which has a pronounced Stokes shift and high \( \Phi_F \) in dimethylformamide (dmf). The compound lases very effectively over a wide turning range (\( \sim 100 \text{ nm} \)) but the limits of this action have yet to be set (refs. 10,11). The bisdimethylamino analogue 14 is markedly less stable in dmf but it too is strongly fluorescent with excellent lasing characteristics. Polarization spectroscopy has shown that phosphorescence is not involved and suggest that the high capacity these compounds have for fluorescence is most likely due to a twisted internal charge transfer (TICT) state (ref. 12). The donation of an electron from the nitrogen non-bonding electron pair to the cyclopropene moiety is not at all untoward. The parent compounds 9 and 12 are known to undergo electrochemical oxidation and reduction to a cation radical and anion radical respectively, which have some 70% of the charge resident in the diarylmethylene moiety (ref. 13). We suggest therefore that \( \Sigma_{le-S} \), excitation is followed by a twisting of, and electron transfer from, the nitrogen atom to give an

![Chart 1](https://example.com/chart1.png)

**Chart 1**

<table>
<thead>
<tr>
<th>( \mu )</th>
<th>( R )</th>
<th>( \mu )</th>
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<th>( \mu )</th>
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<td>H</td>
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<td>H</td>
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<td>Me</td>
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<td></td>
<td>insoluble</td>
<td></td>
<td>Me</td>
<td>1.8 D</td>
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![Figure 1](https://example.com/fig1.png)

**Fig. 1.** Partial infrared spectra (KBr) of (a) 9, (b) 10, (c) 11 and (d) the bis(trimethylammonio) derivative of 11.
Fig. 2. Absorption-emission spectra of 17 in dimethylformamide.

Fig. 3. $^{13}$C Chemical shift correlations for the diarylmethylene cyclopropabenzences.

excited TICT singlet state with the radical centre delocalized into the cyclopropenyl sub-structure. Fluorescence likely leads to the TICT ground state before collapse to the molecular ground state $S_0$.

It is now established that the mesomeric contribution of a functional group and the $^{13}$C chemical shift of an affected carbon can be correlated by linear free energy relationships. Specifically, correlation with the Hammett $\sigma^+_p$ constant, which has a 66% resonance contribution, provides an appropriate measure of changes in $\pi$-electron density over as many as eight bonds (refs. 14,15). The chemical shifts of all the cyclopropabenzynyl as well as the olefinic C1 of atom correlate well as shown in Fig. 3 for C1, C1a(5a) and C2(5) and C1'; equally favourable plots for the naphthalene series are obtained. There is a systematic high field shift of C1, C2(5) and C3(4) and a systematic low field shift of C1' and C1a(5) as the electron donating ability of the remote para-aryl substituent increases. The relative sensitivity of the ring carbon atoms and the $\sigma^+_p$ correlations are fully compatible with increased electron density at C1, C2 and C4 (cf. 1ef) and reduced density at C1' and C1a as expected from mesomerism of the remote substituent.

Crystallographic parameters have been obtained for a number of the compounds and Table 1 lists data for the three-membered ring of 5 and 14 together with those for their parent precursors. The effect of converting C1 from sp$^3$ to sp$^2$ is to widen the C1a-1-5a angle ($\beta$) by $\sim$4° while at the same

<table>
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<th>$b$</th>
<th>$c$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
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<td>R$^1$=R$^2$=H</td>
<td>1.334</td>
<td>1.498</td>
<td>1.367</td>
<td>64.6</td>
<td>52.8</td>
<td>171.7</td>
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<td>1.441</td>
<td>1.385</td>
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<td>62.8</td>
<td>54.4</td>
<td>172.0</td>
<td>-</td>
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<td>1.440</td>
<td>1.352</td>
<td>60.9</td>
<td>58.1</td>
<td>174.5</td>
<td>1.346</td>
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</table>

$^a$Bond lengths in Angstrom units ($\pm 0.003$) and angles in degrees ($\pm 0.2$). Data collected by Dr. R. Boese, University of Essen.

$^b$Exocyclic double bond length.
time the bridge bond α is lengthened by 0.02-0.04 Å; the lateral σ-bonds are markedly shortened (~0.06 Å). The fusion angle γ is widened almost to linearity while α is reduced by 2-3°, but the exocyclic double bond length is essentially unaffected by the changes. It has been noted previously that π-electronic effects are not always mirrored in the geometry of the system (ref. 9). What is obvious here is that the changes recorded reflect the planarization of C1.

Recent chemical studies have encompassed the behaviour of the compounds upon flash vacuum pyrolysis. Cyclopropabenzene undergoes ring contraction to cyclopentadienylidenallene (ref. 16) perhaps as shown below in which Wolf rearrangement of the ring opened carbene is involved. Applied to 1 one might anticipate the formation of the corresponding propatriene:

![Diagram](attachment:image.png)

However, the derivatives 12 and 18 yield complex product mixtures from which only dibenzoacephenanthrylenes (Scheme 3) have been isolated thus far. It is clear that the arylmethylene substitution markedly influences the course of reaction by providing suitably located centres for ring expansion. Diphenyl 9 must undergo dehydrogenation but it is not known whether this precedes the ring closure to give the six-membered ring.

![Scheme 3](attachment:scheme3.png)

The extended conjugation in 1 has prompted an investigation of the behaviour of the derivatives with organometallic reagents (ref. 17). With rhodium the outcome depends upon the nature of the complex. Thus Wilkinson's catalyst leads to carbonyl insertion and the ring expanded metallocycle
19 (X-ray structure) is obtained in high yield. We presume that r-complexation with the exocyclic alkene is followed by ring cleavage and insertion of the metal at the most electronegative centre. By comparison the tris(triphenylphosphine) complex ejects a ligand to give the rhodiacyclobutarene 20. Reaction of 20 with carbon monoxide provides regioselective insertion and the conjugated aryl ketone 21 is obtained by cleavage of the weakest rhodium-carbon bond. Platinum complexes likewise afford platinacyclobutarenes. The results of these and other studies involving these novel hydrocarbons will form the basis of future publications.

Acknowledgement

I am grateful to Professor P. J. Stang (Utah) for his valued collaboration in this area and to our respective co-workers for their skilled assistance. Professor Y. Apeloig (Technion) has kindly shared the results of his calculations and Dr R. Boese (Essen) has conducted crystallographic analyses. I thank them all.

REFERENCES