Ambiphilicity of the Cycloproparenyl Moiety

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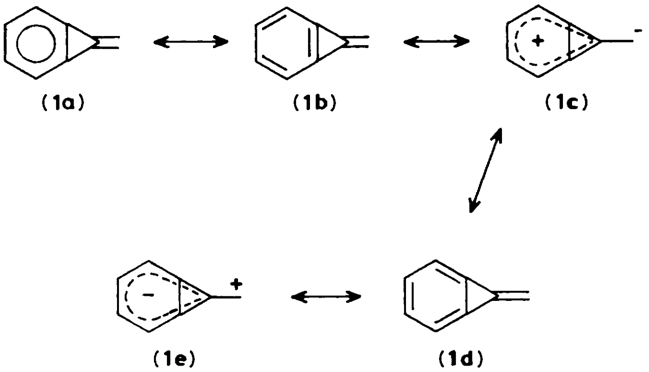
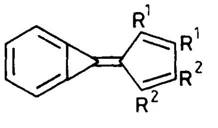
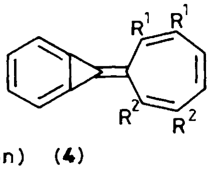
The bis-(*p*-dimethylaminophenyl)methylenecycloproparenes (**8**) and (**9**) are polar compounds with dipole moments which lie in the opposite direction to that in the fluorenylidene analogue (**2**); the mesomerism present in (**8**) and (**9**) is removed upon quaternization of the nitrogen atoms.

It is unusual to find ambiphilicity in organic molecules in general and in simple hydrocarbons in particular. We report that the cycloproparenyl moiety can sustain both positive and negative character, as demonstrated by appropriate derivatives of the recently reported and novel alkyldenecycloproparenes. This type of compound, *e.g.* (**1**), may be regarded as a methylenecycloproparene (**1a**), a benzannelated methylenecyclopropene (**1b**), a novel triafulvene (**1c**), and an unusual radialene (**1d**) all in one.[1] We have reported previously upon the preparation,[2,3] structure,[3] and properties[4] of a range of these remarkably stable hydrocarbons, and shown[5] that contributions to the ground-state structure from the polar form (**1c**) are important. Thus the fluorenylidene derivative (**2**) has a dipole moment of 2.6 D. This compares well with the calculated[6] value of 3.28 D for the unknown parent benzocalicene (**3**) in which the negative end of the dipole lies in the direction of the five-membered ring. We now provide evidence which supports ambiphilic character, as evidenced by the polarites of the calicene (**2**) and the bis-(*p*-dimethylaminophenyl)methylene derivatives (**8**) and (**9**).

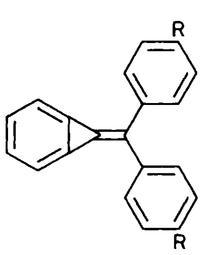


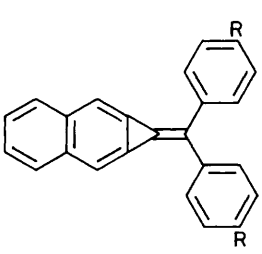
(**1a**) (**1b**) (**1c**)
(**1e**) (**1d**)



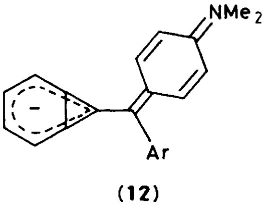


(**2**) $R^1R^1 = R^2R^2$ = benzo(fusion) (**4**)
(**3**) $R^1 = R^2 = H$ (**5**)





(**6**) R = H (**7**)
(**8**) $R = NMe_2$ (**9**)
(**10**) $R = \overset{+}{N}Me_3\ I^-$ (**11**)



(**12**)

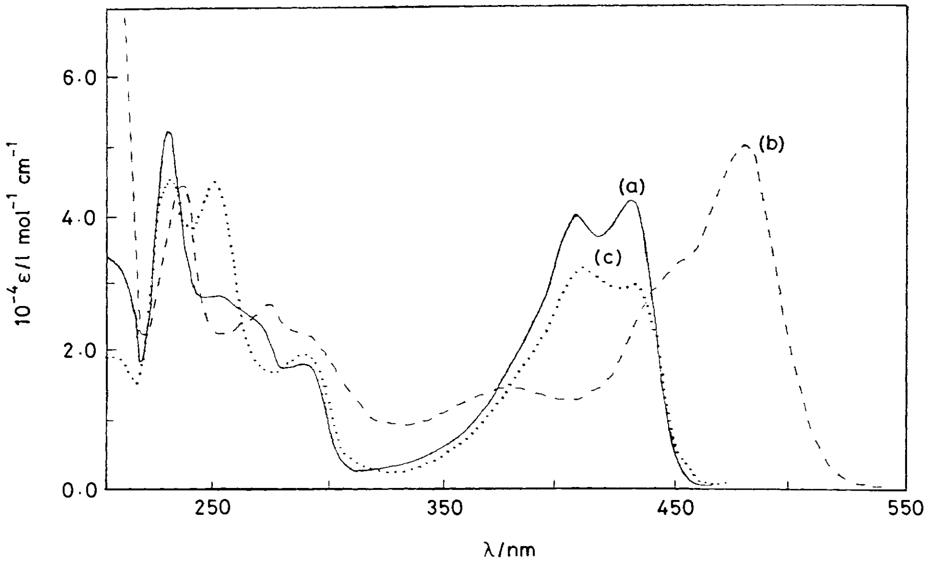


Figure 1. Electronic absorption spectra of (a) 1-diphenylmethylenecyclopropa[*b*]naphthalene (**7**), (b) 1-[bis-(4-dimethylaminophenyl)-methylene]cyclopropa[*b*]naphthalene (**9**), and (c) 1-[bis-(4-trimethylammoniophenyl)methylene]cyclopropa[*b*]naphthalene di-iodide dihydrate, recorded for solutions in acetonitrile.

In the initial search[5] for derivatives of (**1**) with opposite polarities, compounds (**2**) and (**4**) were prepared. Whilst both compounds have permanent dipoles, the direction of that in (**4**) (1.2 D) was far from clear. However, *ab initio* molecular orbital calculations have now shown[6] that in the (unknown) parent benzotriaheptafulvene (**5**) the cycloproparenyl moiety retains positive character, and this same direction of polarization is presumed to be present in (**4**). This is not unusual: species with an electronegative cycloheptatrienylidene unit are known.[7] Unambiguous evidence for negative charge stabilization by the cycloproparenylidene unit, *cf.* (**1e**), comes from the *p*-dimethylaminophenyl derivatives (**8**) and (**9**). These compounds,† prepared in the usual way,[3]‡ have dipole moments[8] of 3.0 and 2.2 D, respectively, and exhibit weak stretching absorptions in their i.r. spectra at *ca.* 1750 cm^{-1}. More importantly, the u.v. absorption maxima of (**8**) and (**9**) are at longer wavelength than those for the unsubstituted analogues (**6**) and (**7**) (Figure 1). Furthermore, the carbon resonances of the cycloproparenyl units in these compounds are modified. The signals for the carbon atoms *ortho* to the site of ring fusion, and that at the cycloproparenylidene centre itself, are shifted upfield§ in (**8**) by 2.1 and 4.8 p.p.m., respectively, in comparison with (**6**), and in (**9**) by 3.4 and 5.9 p.p.m., respectively, in comparison with (**7**). In like manner the diarylmethylene carbon atoms in (**8**) and (**9**) resonate downfield by 1.7 and 2.6 p.p.m., respectively. These data are fully consistent with a significant contribution to the structure from the mesomerically conjugated forms represented by (**12**) in which the cycloproparenyl moiety behaves as an 'electron sink' and delocalizes negative charge.

The mesomerism present in (**8**) and (**9**) is removed upon quaternization of the nitrogen centres. Thus the di-iodides (**10**) and (**11**)¶ display u.v. absorption characteristics remarkably similar to those of (**6**) and (**7**), respectively (Figure 1). The presence of a localized exocyclic double bond in (**10**) and (**11**) is evidenced by a marked increase in the intensity of the i.r. combination band, which is also shifted by *ca.* 25 cm^{-1} to *ca.* 1775 cm^{-1}. This reflects improved coupling between the exocyclic double bond and the aromatic double bond in the three-membered ring.[9] The changes induced by quaternization are also reflected in the ^{13}C n.m.r. spectral data. Shifts in the opposite sense to those recorded for the amines (**8**) and (**9**) are noted. Thus the cycloproparenylidene carbon atoms of (**10**) and (**11**) are deshielded§ by 7.9 and 8.8 p.p.m. and the diarylmethylene sites shielded by 6.0 and 7.1 p.p.m. in comparison with those of (**8**) and (**9**), respectively.

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† Satisfactory analytical and spectroscopic data have been obtained for all new compounds except the trimethylammonium salt (**10**), which decomposed prior to the acquisition of microanalytical data.

‡ Compound (**8**): 24% yield; m.p. 155—157 °C (decomp.) (sealed capillary; N_2). Compound (**9**): 55% yield; m.p. 179—180 °C.

§ All chemical shift differences are taken from data recorded for solutions in $(CD_3)_2SO$.

¶ Compound (**10**): 62% yield; m.p. 214 °C (decomp.) (sealed capillary; N_2). Compound (**11**): 70% yield, as the dihydrate, $C_{30}H_{32}I_2N_2 \cdot 2H_2O$; m.p. 185—186 °C.