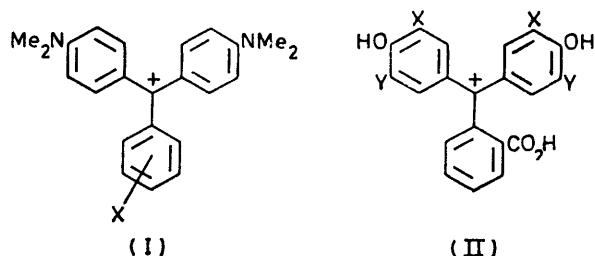


The Electronic Spectra of Diphenylmethyl Carbonium Ions

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The energies of the first band in the electronic absorption spectra of a series of diphenylmethyl cations have been found to correlate with the Taft substituent constants, σ^* . This has led to the prediction of σ^* values for the cyclopropyl, hydroxy-, propynyl, and carboxy-groups.

A CORRELATION has been observed¹ between the energy of the first electronic absorption band near 620 nm and the Hammett σ -value for the substituents on the phenyl ring of Malachite Green (I). A similar correlation has also been found between the energy of the second electronic transition and the Hammett σ -values for 3- and 5-substituents in the hydroxyphenyl rings of a phthalein monocation (II).²



Both transitions are believed to involve the movement of electrons towards the central carbon atom.² In the case of the Malachite Green-type structures, the transition is from the two *NN*-dimethylaminophenyl rings and, in the phthalein, from the carboxyphenyl ring. In both instances placing more electron-withdrawing groups in the rings not directly involved in the transition lowers the energy of the transition.

The electronic spectra of several diphenylmethyl cations have been investigated over a wide range of aqueous sulphuric acid solutions and exhibit negligible solvent shifts.^{3,4} The spectra are of the form shown in Figure 1.

In accordance with previous analyses,^{5,6} the first band in these spectra should correspond to the shift of electrons from the two phenyl rings to the central carbon atom. If this is correct then electron-withdrawing groups attached to the central carbon atom will lower the energy of the transition. It was decided therefore to look for a correlation between the electron-withdrawing ability in the form of the Taft polar substituent constants σ^* and the energy of the highest-wavelength transition (see Table 1). The system chosen, $\text{Ph}_2\text{C}^+\text{X}$, had no substituents in the two phenyl rings.

The value of ρ^* , obtained from the slope of the plot of the transition energy versus σ^* (see Figure 2), is $-2.43 \times 10^3 \text{ cm}^{-1}$ (correlation coefficient 0.91). This is

¹ C. C. Barker, M. H. Bride, G. Hallas, and A. Stamp, *J. Chem. Soc.*, 1961, 1285.

² A. C. Hopkinson and P. A. H. Wyatt, *J. Chem. Soc. (B)*, 1970, 530.

³ N. C. Deno, J. Jaruzelski, and A. Schriesheim, *J. Org. Chem.*, 1954, **19**, 155.

larger than the ρ values for phenolphthaleins² ($-1.27 \times 10^3 \text{ cm}^{-1}$), phenolsulphonophthaleins² ($-1.36 \times 10^3 \text{ cm}^{-1}$), and the Malachite Green ions¹ ($-6.5 \times 10^2 \text{ cm}^{-1}$),

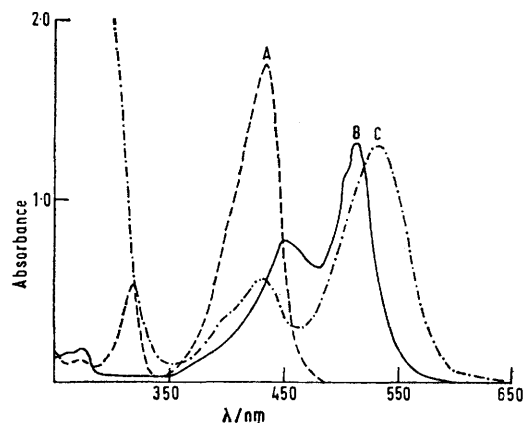


FIGURE 1 Electronic absorption spectra of some typical diphenylmethyl cations, $\text{Ph}_2\text{C}^+\text{X}$: A, X = Et; B, X = $\cdot\text{C}_i\text{CPh}$; C, X = CO_2Me

indicating that the introduction of electron-donating groups into the diphenylmethyl carbonium ions has a greater effect than their introduction into the phenolphthaleins, the phenolsulphonophthaleins, and the Malachite Green ions.

TABLE I

Spectral data for diphenylmethyl carbonium ions, $\text{Ph}_2\text{C}^+\text{X}$

X	σ^* ^a	Highest observed wavelength, $\lambda_{\text{max.}}/\text{nm}$	$\log \epsilon$	Energy of transition ($\times 10^{-4} \text{ cm}^{-1}$)
Me	0.00	425 ^b		2.353
H	0.49	440 ^b		2.273
Et	-0.10	432 ^c	4.54	2.315
Pr ⁱ	-0.19	432 ^c		2.315
Ac	+1.65	530	3.52	1.888
CH ₂ CHPh	+0.41	436	3.60	2.294
CH ₂ Ph	+0.22	432 ^b		2.315
CH ₂ OPh	+0.85	448	3.23	2.232
C ₆ H ₅	+1.35	513	4.78	1.949
CO ₂ Me	+2.00	535	3.78	1.869

^a Ref. 7. ^b V. Gold and F. L. Tye, *J. Chem. Soc.*, 1952, 2172. ^c A. G. Evans, P. M. S. Jones, and J. H. Thomas, *J. Chem. Soc.*, 1957, 104.

The spectra of other substituted diphenylmethyl carbonium ions and the computed best line from Figure 2

⁴ M. S. Newman and N. C. Deno, *J. Amer. Chem. Soc.*, 1951, **73**, 3644.

⁵ H. C. Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 275.

⁶ R. Grinter and S. F. Mason, *Trans. Faraday Soc.*, 1964, **60**, 264.

were used to predict σ^* values for several groups (see Table 2).

The predicted σ^* value for the cyclopropyl group is slightly positive indicating that the cyclopropyl ring is

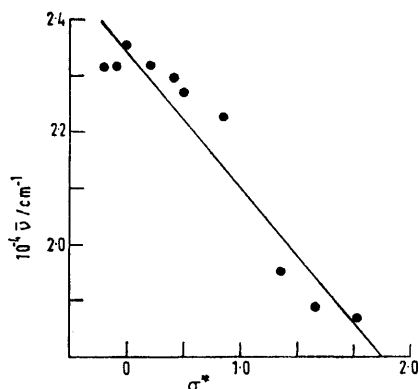


FIGURE 2 A plot of the energy of the first electronic absorption band versus σ^*

slightly electron-withdrawing. The hydroxy-group is a very good electron-donating group and, consistent with this, is found to have a fairly large negative value of σ^* .

TABLE 2

Spectral data for other diphenylmethyl carbonium ions Ph_2CX^+ and the predicted σ^* values for the corresponding substituents X.

X	Highest observed wavelength, $\lambda_{\text{max.}}/\text{nm}$	$\log \epsilon$	Energy of transition ($\times 10^{-4} \text{ cm}^{-1}$)	Predicted σ^* (± 0.23)
Cyclopropyl	436	4.16	2.293	+0.21
OH	344 ^a	4.89	2.907	-2.32
C≡CMe	462 ^a		2.165	+0.73
CO ₂ H	543	3.82	1.842	+2.06

^a G. A. Olah, C. V. Pitman, jun., R. Waak, and M. Doran, *J. Amer. Chem. Soc.*, 1966, **88**, 1488.

The σ^* value of +0.73 for propyne is less than that of phenylacetylene, reflecting the more electron-withdraw-

⁷ J. Hine, 'Physical Organic Chemistry,' McGraw-Hill, 1962, pp. 85, 97.

⁸ D. Ioffe, *Zhur. obshchei Khim.*, 1965, **35**, 1851.

ing nature of the phenyl group. Finally, the Hammett σ value for the carboxy-group is slightly larger than that for the methyl ester.⁷ This trend is again shown with the predicted σ^* for the carboxy-group of +2.06 which is slightly larger than the value of 2.00 for the methyl ester groups.

EXPERIMENTAL

The electronic spectra were measured on a Unicam SP1800 spectrophotometer with stoppered 10-mm quartz cells. The carbonium ions were produced by dissolving the corresponding alcohol in 96% sulphuric acid.

Materials.—Methyl benzyloate, benzyloic acid, and cyclopropyldiphenylmethanol were obtained commercially.

1-Hydroxy-1,1-diphenylpropan-2-one was prepared by the method of Ioffe⁸ as needles, m.p. 62–63° (lit.,⁹ 58–60°) (from hexane).

1,1,3-Triphenylprop-2-yn-1-ol was prepared by the action of phenylethynylmagnesium bromide on benzophenone as needles, m.p. 78–80° (lit.,¹⁰ 79°) (from ethanol-water).

1,1,3-Triphenylprop-2-en-1-ol was prepared by the catalytic reduction of 1,1,3-triphenylprop-2-yn-1-ol over Lindlar catalyst in ethyl acetate. The catalyst was filtered off, the solvent was removed, and the residue was dissolved in benzene and stirred with a catalytic amount of iodine for 24 h. The iodine was removed by washing the benzene solution with sodium thiosulphate solution and the benzene layer was separated, dried (MgSO₄), and evaporated. 1,1,3-Triphenylprop-2-en-1-ol, needles, had m.p. 95–98° (lit.,¹¹ 104–106°) (from hexane).

2-Phenoxy-1,1-diphenylethanol was prepared by the reaction of phenylmagnesium bromide (0.02 mol) with methyl phenoxyacetate (0.1 mol) in dry ether, as plates, m.p. 97–99° (from ethanol-water) (Found: C, 83.1; H, 6.22. C₂₀H₁₈O₂ requires C, 82.75; H, 6.25%), *m/e* 273 (*M* – OH).

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⁹ C. A. Buchler, H. A. Smith, K. V. Nayak, and T. A. Magee, *J. Org. Chem.*, 1961, **26**, 1573.

¹⁰ J. Baltes and F. Volbert, *Fette, Seifen, Anstrichm.*, 1955, **57**, 660.

¹¹ I. N. Rozhkov and S. M. Makin, *Zhur. obshchei Khim.*, 1964, **34**, 59.