of each ketone (I–IV) with cyclopentadiene in methylene chloride containing aluminum chloride[6] (0.3 mole) at 0–10° gave in every case a good yield of two stereoisomeric ketones (*exo* addition always predominating). In the diene series of adducts the isomer formed from both *endo*- (I) and *exo*-dicyclopentadienone (II) must be *endo,trans,exo* (VI); the configurations of the other two isomers then follow. In the dihydro series all four adducts are, of course, different, but the two *endo,trans,exo* isomers were easily identified by hydrogenation to the same saturated ketone, identical with the tetrahydro derivative of VI. Similarly, hydrogenation related V to VIII and VII to XI. For identification the melting points of the isomers are given under the formulae and their ultraviolet spectra are summarized in Table I. All the compounds had the expected elemental composition and infrared and nmr spectra.

Table I. Spectra of Dicyclopentadienones

Structure and Configuration	λ_{max}, mμ^a	ϵ_{max}
III, *endo*	228	7850
	323	38
IV, *exo*	226	8250
	320.5	61
I, *endo*	226	7400
	323	36
II, *exo*	216.5	7390
	247.5[b]	1070
	323	48
VIII, *endo,trans,endo*		
	303	27.5
X, *endo,trans,exo*		
	302.5	37
IX, *exo,trans,endo*	224	1330
	307	79
XI, *exo,trans,exo*	224	1310
	309	84
V, *endo,trans,endo*		
	302	33.5
VI, *endo,trans,exo*	221	1410
	308	83
VII, *exo,trans,exo*	225	2540
	309	137

^{a} Maxima of solutions in ethanol at wavelength longer than 210 mμ. ^{b} Shoulder.

The *exo,trans,exo* isomer VII was identical with the ketone from bicyclo[2.2.1]heptadiene and iron carbonyl.[7] The second double bond in the diene is not therefore involved in the reaction as we once thought,[1] but merely serves to increase the strain in the first and thus its reactivity. *exo* addition then occurs, as in the reaction with aqueous nickel carbonyl.[8] Indeed, some of the tetrahydro derivative of VII is formed when bicyclo[2.2.1]heptene reacts with iron carbonyl.

The chemistry of these compounds, including the rates of solvolysis of esters of the alcohols, will be reported later.

(6) R. O. Williams, Ph.D. Thesis, Southampton University, 1961; P. Yates and P. Eaton, *J. Am. Chem. Soc.*, 83, 4436 (1960); R. Robinson and G. I. Fray, *ibid.*, 83, 249 (1961).

(7) The configurations of the other ketones mentioned in ref 1 should also be revised from *endo* to *exo*.

(8) C. W. Bird, R. C. Cookson, J. Hudec, and R. O. Williams, *J. Chem. Soc.*, 410 (1963).

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σ-Coupled p Electron Systems. A New Type of Chromophore

Sir:

Intense absorption of light in the near-ultraviolet region of the spectrum by compounds of the lighter elements generally involves electronic transitions on chains of three or more atoms having parallel p orbitals (dienes, enones, vinylamines, etc.) A second category was recognized more recently[1] in which the orbitals concerned are not on adjacent atoms (intramolecular charge transfer), and many further examples have since been described.[2] We now wish to draw attention to a third category which has remained unrecognized, namely σ-coupled transitions.[3,4]

Consider, for example, a 1,5-diene in a conformation where the central 3-4 bond is in a plane at right angles to both double bonds (B). The two π systems will be

B
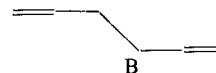
coupled by overlap with the central 3–4 σ bond, splitting both the π and π* levels and leading therefore to four possible transitions.[5]

The transition from the higher energy π to the lower energy π* orbital will then be shifted to longer wavelengths than in simple olefins, but this transition should be very sensitive to the precise geometry of the system. The coupling will decrease as the 3–4 bond is moved out of the plane normal to the double bond, until it is abolished when the 3–4 bond lies in the plane, and the spectrum will then become that of a normal olefin. Various classes of such coupled chromophores can be imagined, according to how the p orbitals at each end of the system are provided; *e.g.*, the C=C bonds might be replaced by C=O, N=N and so on, or by atoms with unshared electron pairs such as N or S. In unsymmetrical compounds the transition would have an element of charge transfer, which should become very marked in extremes such as β-amino ketones.

There are cases of what we believe to be such transitions in the region 220–260 mμ among hydrocarbons, γ,δ-unsaturated carbonyl compounds, γ,δ-unsaturated amines, and β-amino and β-thio ketones, some examples of which are given below.

The spectra of some ketones which demonstrate the exacting spatial requirement are summarized in Table I in the preceding communication. Among those with with two bicycloheptane units (V–XI) only those containing the cyclopentanone ring *exo* to a bicycloheptene (VI, VII, IX, XI) show an additional band at

(1) R. C. Cookson and N. Lewin, *Chem. Ind.* (London), 984 (1956).

(2) *Inter alia*, H. Labhart and G. Wagniére, *Helv. Chim. Acta*, 42, 2219 (1959); H. Birnbaum, R. C. Cookson, and N. Lewin, *J. Chem. Soc.*, 1224 (1961); R. C. Cookson and S. MacKenzie, *Proc. Chem. Soc.*, 423 (1961); S. Winstein, L. de Vries, and R. Orloski, *J. Am. Chem. Soc.*, 83, 2020 (1961); N. J. Leonard, T. W. Milligan, and T. L. Brown, *ibid.*, 82, 4075 (1960).

(3) In the π → π* transitions of both the classical conjugated systems and those showing intramolecular charge transfer the σ bonds play no essential part in the transition, they merely hold the atoms together. In this new type of transition a σ bond is an integral part of the chromophore undergoing the transition.

(4) We originally referred to the excited state as σ*, since it has a node through the central single bond, but changed the description after helpful correspondence with Professor R. Hoffmann (Cornell), whom we thank for his interest.

(5) This elementary treatment neglects the more or less extensive mixing with other orbitals of appropriate symmetry that occurs in real molecules.

about 223 mμ, each such combination contributing ϵ_{max} of about 1300. The *endo* combination (V, VIII, X) produces no additional absorption in the accessible
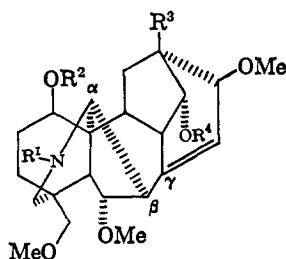
XIIa, R^1 = Et, R^2 = H, R^3 = H, R^4 = H
b, R^1 = Et, R^2 = Ac R^3 = H, R^4 = Ac
c, R^1 = Me, R^2 = Me, R^3 = OH, R^4 = H
d, R^1 = Et, R^2 = Me, R^3 = H, R^4 = H
e, R^1 = Et R^2 = Me, R^3 = OH, R^4 = H

XIII   XIV   XV

E = CO$_2$Et
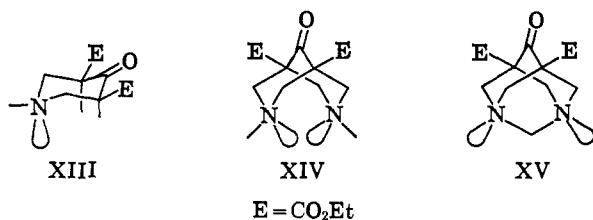
region of the spectrum, and the double bond and carbonyl group must be too far apart for direct charge transfer.[1,2] Only in the *exo* isomers are the olefin and carbonyl groups in approximately parallel planes (almost the ideal extended arrangement); the change in dipole moment during the transition is less in the *endo* isomers, and the energy gap is increased by bonding overlap between orbitals on nonadjacent atoms in the ground state and antibonding overlap in the excited state (particularly around the *endo* face of the carbon of the carbonyl group and the nearer carbon atom of the double bond). The longer wavelength of the extra band in *exo*-dicyclopentadienone (II) corresponds with the longer σ-coupled system; the excitation probably mainly involves the σ bond γ to the cyclopentenone carbonyl group rather than α' as in the other ketones.

In *n*-hexane these bands moved to shorter wavelengths, suggesting that the excited state is more polar than the ground state, and the n $\rightarrow$ π^* bands moved to longer wavelengths and developed marked vibrational structure (four to six components being resolved).

In the pyro derivatives of the aconite alkaloids (XII) the molecule is ideally set up for a σ-coupled transition; the electron pair on the nitrogen atom, the α,β bond, and the p orbital on C$_\gamma$ are almost exactly in the same plane and parallel to one another.[6] In fact, pyroneoline[7] (XIIa), pyrodelphonine[7] (XIIc), pyrochasmanine[8] (XIId), and pyrobikhaconine[8] (XIIe) all show an unexpected absorption maximum at about 245 mμ (ϵ ~6000), which is abolished by protonation of the nitrogen atom or amide formation (R = CHO or MeCO) (see Table I).

(6) In this case as well as in the bicyclo[2.2.1]heptene derivatives, the energy of the ground state is raised to some extent by strain (an effect that would be much enhanced in a *trans*-1,2-disubstituted cyclopropane of correct geometry), but this bonus is not necessary, as shown by the strainless XV.

(7) K. Wiesner, H. W. Brewer, D. L. Simmons, D. R. Babin, F. Bickelhaupt, J. Kallos, and T. Bogri, *Tetrahedron Letters*, No. 3, 17 (1960).

(8) O. Achmatowicz, Y. Tsuda, L. Marion, T. Okamoto, M. Natsume, H.-H. Chang, and K. Kajima, *Can. J. Chem.*, **43**, 825 (1965).

Table I. Chromophores Containing Nitrogen and Sulfur

Compd	λ_{max}, mμ	ϵ_{max}	Ref
XIIa	236	7100	7
XIIb	243	5600	7
XIIc→	245	6300	7
XIId	244	5500	8
XIIe	249	5100	8
XIII			9
XIV			9
XV	262	3600	9
Tropinone	231.5	400	
Tropinone^a	243	445	
4-Thiacyclohexanone	235	350	10

^{a} In *n*-hexane; others in ethanol.

The geometrical requirements are even more dramatically illustrated by the piperidones[9] XIII–XV. XIV and XV differ in this connection only in that the electron pairs and alkyl substituents on the nitrogen atom have changed places:[11] the electron pairs in XIV are axial and in XV equatorial. Only the latter can overlap effectively with the α,β bond, so a strong band is expected for XV but none for XIV. This is amply borne out by the facts.[9] The amines with axial electron pairs (XIII and XIV) show no intense absorption in the accessible ultraviolet region, whereas XV has a strong band at 262 mμ which disappears in acid solution.

The contrasting effect of polarity and hydrogen-bonding ability of solvents on $\pi \rightarrow \pi^*$ and n $\rightarrow$ π^* transitions has been widely used in distinguishing between the two classes.[12] No general rule applies to σ-coupled transitions. As an example, let us compare the behavior of the unsaturated ketones and the amino ketones. Change from *n*-hexane to ethanol shifts the absorption of the *exo*-ketones in Table I to *longer* wavelengths, but the analagous change from acetonitrile to ethanol shifts the band of XV to *shorter* wavelengths.[9] Basic strength and hydrogen-bonding ability increase in the series C=C < C=O (n electrons) ≪ N. Thus, although the transition involves transfer of charge toward C=O in both cases, in the *exo*-ketones the energy of the excited state is lowered on changing the solvent to ethanol (C=O hydrogen bonded, C=C hardly effected), giving the red shift, while in XV the energy of the ground state is lowered (C=O only weakly hydrogen bonded, N strongly H-bonded), producing the blue shift.

Similar considerations of orbital overlap in the transition state explain the stereospecificity for acceleration of fragmentation reactions.[13] However, the equilibrium conformation of the electron pair on nitrogen (when it is free to invert) does not necessarily affect

(9) J. Kuthan and J. Palecek, *Collection Czech. Chem. Commun.* **28**, 2260 (1963).

(10) E. A. Fehnel and M. Carmack, *J. Am. Chem. Soc.*, **71**, 84 (1949).

(11) The conformation of the diazaadamantanone (XV) is, of course, fixed. No doubt the two chair rings in XIV are slightly flattened by repulsion between the nitrogen atoms, but such minor distortions do not affect the main argument. The slight inflections in the end absorption at about 245 mμ, obvious in the spectrum of XIV and barely visible in that of XIII, may come from very small equilibrium concentrations of molecules in conformations (*e.g.*, the boat–chair of XIV) with axial methyl groups. Application to conformational analysis of structures such as tropinone will be considered later.

(12) For references see H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 186.

(13) C. A. Grob, *Bull. Soc. Chim. France*, 1360 (1960); O. E., Edwards, *Chem. Commun.*, 318 (1965).

the rate of the fragmentation solvolysis,[14] whereas the Franck–Condon principle makes it of vital importance in the electronic excitation.

(14) C. A. Grob, H. R. Kiefer, H. Lutz, and H. Wilkens, *Tetrahedron Letters*, 2901 (1964).

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Internal Reflection Spectroscopic Observation of Electrode–Solution Interface

Sir:

We wish to report the use of internal reflection spectroscopy to *directly observe* and *monitor in situ* the *surface* concentration of the product of an electrochemical reaction. An optically transparent glass electrode coated with tin oxide was used. The optical configuration was similar to those previously described.[1]
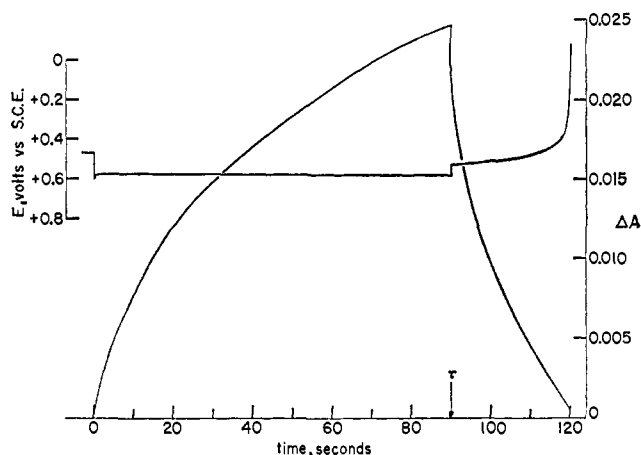

Figure 1. $E - t$ and $\Delta A - t$ behavior for solution 5 mF in o-tolidine and 0.1 F HCl. The electrolysis current of 1.0 ma results in the oxidation of I to II at the electrode surface to time τ, when current reversal causes reduction of II to I. The electrode area is approximately 13 cm².

The absorption of the oxidation produt (II) of o-tolidine (I) in 0.1 F HCl solution was monitored at 4380 A. Simultaneous electrochemical and normal transmittance spectroscopic studies of o-tolidine at tin oxide coated glass electrodes have been carried out.[2]
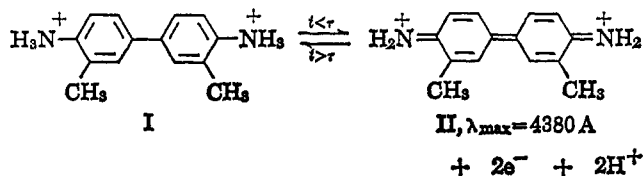
Plots of the voltage–time and absorbance–time characteristics during constant-current electrolysis (chronopotentiometry) are shown in Figure 1. To

(1) W. N. Hansen and J. A. Horton, *Anal. Chem.*, **36**, 783 (1964).
(2) T. Kuwana, R. K. Darlington, and D. W. Leedy, *ibid.*, **36**, 2025 (1964); F. A. Schultz and T. Kuwana, to be published.
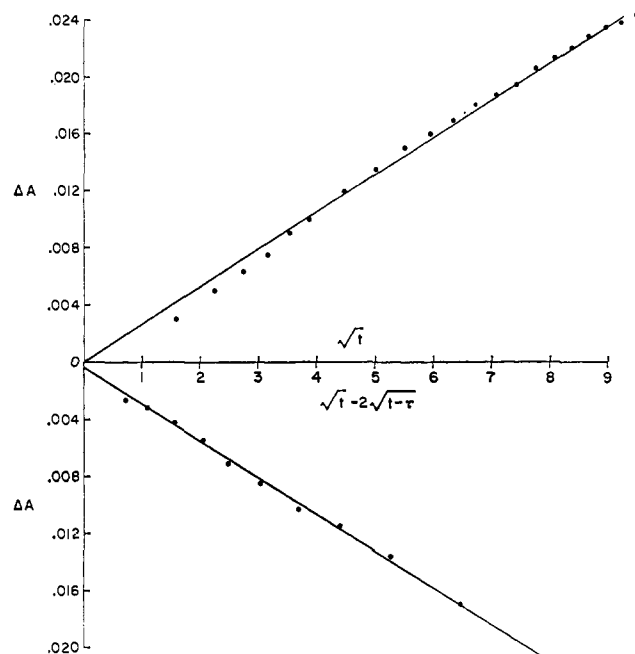

Figure 2. Plot of ΔA vs. $\sqrt{t}$ and $\sqrt{t} - 2\sqrt{t - \tau}$. Abscissa units are sec$^{1/2}$; slopes are 0.0026 and 0.0027 sec$^{-1/2}$ for ΔA vs. $\sqrt{t}$ and $\sqrt{t} - 2\sqrt{t - \tau}$, respectively.

time τ the oxidation of o-tolidine results in the formation of II at the electrode surface; at time τ the current is reversed and reduction of the *product* II now occurs. The surface concentration of product II for time $t < \tau$ is proportional to $t^{1/2}$, and for time $t > \tau$ is proportional to the quantity $[t^{1/2} - 2(t - \tau)^{1/2}]$.[3] From the linearity of the plots of these quantities in Figure 2, it is clear that only a region *very close* to the electrode surface is being observed. It is estimated that the penetration depth into the solution from the surface of the electrode is *ca.* 2000 A. The penetration depth is here defined as the distance in solution at which the square of the amplitude of the electric field has decreased to 10% of its value at the surface.

The calculated "effective" path length of between 24,000 and 28,000 A for the multiple reflection cell used agrees well with a value of *ca.* 25,000 A obtained from the experimental absorbancy using a molar absorptivity of 50,000 l./mole/cm for product II at a wavelength of 4380 A.[2]

The possible application of internal reflection spectroscopy to electrochemistry suggested earlier[4] was recently investigated in the infrared region using germanium electrodes.[5] The work reported here is, however, to our knowledge the first in which it has been conclusively demonstrated that the *surface* concentration, well within the diffusion layer, may be directly observed. Results from chronoamperometry and sweep voltammetry using this technique support our conclusion. Further experimental work is in progress

(3) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, Chapter 8.
(4) W. N. Hansen, L. Lynds, and R. A. Osteryoung, "Infrared Reflectance Study of Gas–Solid Interaction," Final Summary Report, Oct 1962, Contract No. DA-44-009, U. S. Army Engineers Research and Development Laboratories, Fort Belvoir, Va.; Proceedings of the ARPA Fuel Cell Conference, Whiting, Ind., Feb 1962.
(5) H. B. Mark, Jr., and B. S. Pons, *Anal. Chem.*, **38**, 119 (1966).