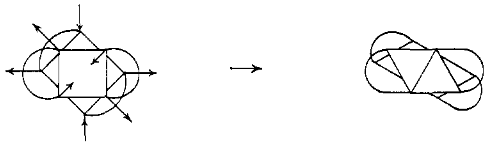
group was ascertained to be Pbcn with four molecules per unit cell.

Using the equiinclination Weissenberg technique, intensity data were collected for successive layers 0*kl* through 6*kl* using Cu Kα radiation. The intensities were estimated visually against a calibrated strip prepared from the same crystal. Absorption and anomalous dispersion corrections were applied along with the usual Lorentz-polarization corrections and, after placing the data on an absolute scale by Wilson's method, a three-dimensional Patterson function was computed. From the Patterson map, both the cesium and yttrium atoms were located on twofold axes in the crystal. The rest of the structure was solved by successive least-squares and Fourier calculations.[8] At the present stage of refinement, the conventional *R* factor[9] is 0.14 for 750 observed reflections. The individual isotropic temperature factors for the fluorine atoms range from 12 to 20 A^2, and, in addition, there is evidence for rotational disorder of the trifluoromethyl groups on the difference Fourier maps.

The basic structure of the $[Y(HFA)_4]^-$ anion is shown in Figure 1. Eight oxygen atoms surround the central yttrium atom at an average distance of 2.33 ± 0.04 A in a dodecahedral configuration. The angular dodecahedral parameters,[10] θ_A and θ_B, are 40 ± 2 and 67.5 ± 2°, respectively. Unlike all other dodecahedral complexes known to contain four bidentate chelating ligand molecules, however, the β-diketonate groups span the *g* edges of the dodecahedron rather than the *m* edges,[10] resulting in over-all idealized D_2 symmetry for the anion.[11] Although it is at present not possible to provide a detailed explanation for this behavior, it is interesting to note that the D_2 dodecahedral structure found for the $[Y(HFA)_4]^-$ ion may be derived from the D_2 antiprismatic structure, I, *via* a slight distortion of the latter structure in the manner shown below. One possible cause of this distortion might be the close association of the Cs$^+$ ions with the $[Y(HFA)_4]^-$ anions found to occur in the crystal structure, for each cation is surrounded by eight fluorine atoms from two neighboring anions (Cs–F, 3.3 A). Taken collectively, these cations serve to link together infinite columns of discrete dodecahedral $[Y(HFA)_4]^-$ ions in the lattice. This packing interaction may also be related to the unusual volatility[3] of the compound.



I, D_2 antiprismatic III, D_2 dodecahedral

Other X-ray crystallographic studies are currently in progress to explore further the possibility that geometric isomerism might occur in certain eight-coordinate β-diketonate Y(III) complexes.

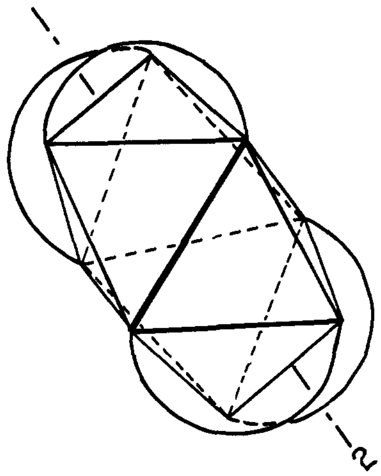


Figure 1. Schematic representation of the structure of the $[Y(HFA)_4]^-$ ion, assuming idealized D_2 symmetry. Half-circles indicate the pattern of ring attachment. The crystallographically required twofold axis is also shown.

Acknowledgments. We wish to thank Dr. S. J. LaPlaca for kindly informing us of his structural results prior to publication, the National Science Foundation for partial support of this research through Grant No. GP-4329 and for a Postdoctoral Fellowship (S. J. L.), and the Woodrow Wilson Foundation for fellowship aid (P. L.)

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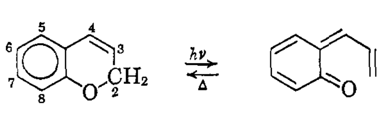
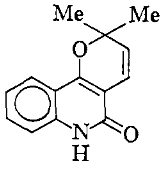
Photochromism of Synthetic and Naturally Occurring 2H-Chromenes and 2H-Pyrans

Sir:

In the course of investigation of spectroscopic and photochromic properties of 1,3,3-trimethylindolinobenzospiropyran and its derivatives,[1] 2H-chromene (I) and a number of its simple derivatives were synthesized or obtained from other sources.



I II



III

We wish to report that the latter compounds are photochromic and propose structure II for the colored form. This seems to be the only logical possibility and is in agreement with the following observations. Photochromism was observed in over 25 molecules, irrespective of the presence, location, and nature of

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(8) Programs for the IBM 7094 used in this work, in addition to various local programs written at the Brookhaven National Laboratory and kindly made available to us, were Burnham's GNABS absortion program, Zalkin's FORDAP Fourier program, and the Busing–Levy ORFLS least-squares program and ORFFE error function program.

(9) Defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$.

(10) *Cf.* J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 2, 235 (1963), for a definition of the nomenclature used here.

(11) Recently, M. Cefola, W. Hamilton, R. Lalancette, and S. LaPlaca (to be published) have determined the crystal structure of $NH_4[Pr(TTA)_4] \cdot H_2O$ (TTA = thenoyltrifluoroacetonate) and also find the ligand molecules to span the same four dodecahedral *g* edges. The over-all symmetry in their anion is less than D_2, however, since the attachment of one of the four asymmetric TTA ligand molecules is reversed from that of the other three.

(1) R. S. Becker and J. K. Roy, *J. Phys. Chem.*, 69, 1435 (1965).

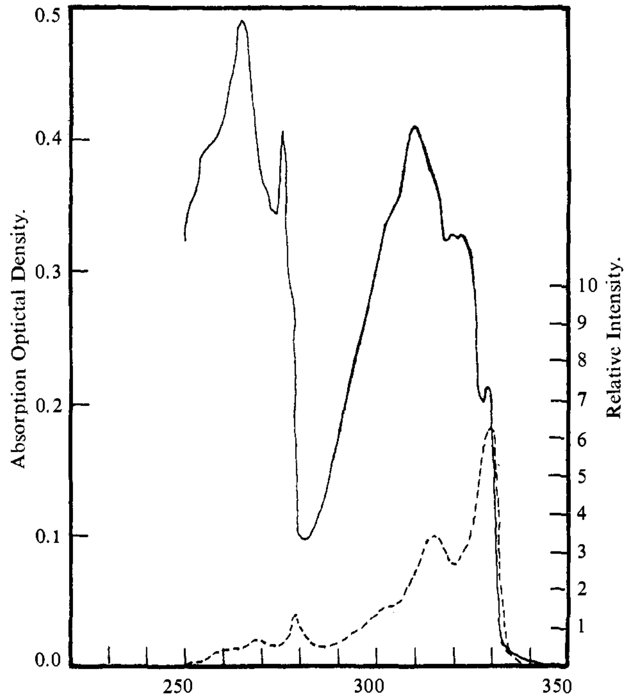

Figure 1. Absorption (———) and excitation spectra (---------) of 2,2-diethylchromene at 77°K in 3-methylpentane.

substitution or benzo condensation, as long as the chromene unit was present. Benzo annelation in positions 5,6 or 7,8 increases the stability of the colored form; benzo annelation in 6,7 decreases it. Conjugative substituents in position 2 also increase the stability of the colored form, and bulky substituents in position 4 decrease it. The colored form of 2,2-diphenyl-5,6-benzochromene rapidly disappears on addition of tetracyanoethylene, as expected for the proposed structure. Investigations on direct evidence supporting the proposed structure of the colored species are in progress. The proposed mechanism is consistent with the usual interpretation[2] of the photochromism of spiropyrans as involving a rupture of a C–O bond in the chromene portion of the molecule. Of particular importance is the fact that the present finding, proving that the chromene-only half of the spiropyrans is photochromic, gives credence to the mechanism proposed for the spiropyrans. A somewhat related case of a rapid thermal equilibrium between a dienone and a pyran has been reported recently.[3]

Conversion from the colorless to the colored form is effected by ultraviolet irradiation at low temperatures in fluid or rigid solution in a variety of solvents or in a plastic. In some cases, colorless → colored conversion can be accomplished at room temperature. Generally, the color gradually disappears on warming up to room temperature, although sometimes the colored product is stable at and even above room temperature. The process may be repeated many times but it is not always completely reversible, particularly in the presence of oxygen. The side reactions and/or photoreactions vary with substitution and are being investigated. The highest temperature at which photoconversion can be effected as well as the thermal stability of the colored form (up to several hours at room temperature) are strongly dependent on substitution. A variety of colors were observed, most often yellows, oranges, and reds.

The colorless pyran III behaves in a similar fashion, thus strongly supporting the mechanism proposed. Accordingly, it seems that reversible photochemistry is not limited to 2H-chromene and its derivatives, but is a general property of molecules with the 2H-pyran skeleton. The colored form of III is only very pale yellow, as expected when the same mechanism is in operation since it now contains no quinoid chromophore.

Absorption spectra of the colored forms of the chromenes exhibit a broad band in the visible region (400–600 mμ), with poorly resolved fine structure, and a series of sharp peaks in the ultraviolet. The differences in color from one compound to another appear to be mainly due to variation in the relative intensities of the individual vibrational components of the visible band rather than to shifts of the band as a whole.

Spectroscopy of the colorless form of 2,2-diethylchromene in 3-methylpentane solvent was investigated in more detail. At 77°K the longest wavelength absorption band is partially resolved into vibrational components. Efficiency of ultraviolet fluorescence emission is high if the wavelength of the exciting light corresponds to the first vibronic peak in the absorption spectrum (the 0–0 band) but decreases sharply if shorter wavelengths are used (see Figure 1). On the other hand, efficiency of color formation seems to be much lower for excitation into the 0–0 band than for excitation into the higher vibrational components. Phosphorescence, if present at all, is very weak.

To our knowledge, the foregoing is the first observation of the fact that a photochemical reaction of an organic compound may require at least one quantum of vibrational energy in the first excited singlet state. Three explanations are possible: (1) the potential energy curve corresponding to a vibrational mode involved has a very shallow minimum in the lowest excited singlet state such that C–O bond dissociation occurs on vibronic excitation but not on a purely electronic excitation; (2) a dissociative state crosses the lowest excited singlet state at or near the first vibrational level; (3) the molecular rearrangement occurs in the triplet state, and in order to cross from the lowest excited singlet state into the triplet manifold the molecule requires at least one quantum of vibrational energy. Explanations 2 and 3 could be identical if the dissociative state were a triplet. This highly interesting phenomenon has also been noticed in some photochromic spiropyrans[4] and is being studied further.

With the establishment of photochromism in synthetic chromenes, it appears significant to report that a similar phenomenon exists in naturally occurring ones.

Thus far, nine chromene derivatives and one pyran have been investigated, and all are photochromic. These include a wide variety of structures, including lapachenole, evodione, xanthyletin, and alloevodionol. The pyran examined was flindersine (III).

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(2) R. Exelby and R. Grinter, *Chem. Rev.*, **65**, 247 (1965).

(3) E. N. Marvell, G. Caple, T. A. Gosink, and G. Zimmer, *J. Am. Chem. Soc.*, **88**, 619 (1966).

(4) R. S. Becker and J. K. Roy, unpublished, University of Houston, 1965.

The photochemistry can be done in rigid medium at liquid nitrogen temperature, in fluid solution at low temperature (−20 to −196°), and at room temperature. Not all can be converted to a photochemical colored form at room temperature but, for example, lapachenole can. Further, in the latter case reversibility exists for several cycles, but after these, the colored form remains with little fading. Some compounds can be converted at low temperature and not completely fade when warmed to room temperature, as, for example, alloevodionol and lapachenole. The photochemical colored forms vary in color, being shades of yellow, pink, green, and violet. The colored form of the pyran is yellow.

The importance of this discovery is the implication of such photochemical behavior in plant systems. Chromenes and pyrans occur in a wide variety of sources, including leaves.[5] Thus, the roles of these chemical classes can be conceived to be as (1) photochemical memory storage devices and (2) precursors to synthesis of more complex molecules through the photochemical production of a reactive colored form. Further subtopical considerations include their role in regulatory processes, such as growth, germination, budding, fruiting, photoperiodisms, and phototropism.

More detailed investigation of the spectroscopy and photochemistry of the chromenes and pyrans, as well as other molecules, is in progress. It could be anticipated that investigation of these systems would open exciting new avenues of understanding of plant processes. It is hoped that this communication, in part, will stimulate such studies.[6]

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(5) F. M. Dean, "Naturally Occurring Oxygen Ring Compounds," Butterworth and Co. (Publishers) Ltd., London, 1963.

(6) We wish to acknowledge the generosity of several people for samples of compounds. Individual acknowledgement will be given in later publications. This research was sponsored by the U. S. Air Force, Systems Engineering Group, Wright-Patterson Air Force Base, Ohio, Contract AF 33(615)-1733.

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Some Chemistry of the C_2 Molecule

Sir:

During studies of the reactions of carbon vapor with alcohols and halocarbons, large quantities of acetylene and smaller quantities of ethylene have been observed. This is in marked contrast to work in this laboratory with olefins[1] and hydrocarbons,[2] where little or no acetylene and ethylene are observed.

Acetylene has been reported in reactions involving "hot" carbon atoms with olefinic hydrocarbons,[3] saturated hydrocarbons,[4,5] and alkyl halides.[5] In these cases acetylene is formed by insertion or addition of energic ^{11}C atoms followed by fragmentation of the "hot" intermediate to acetylene and other products.

Under our conditions, condensed-phase, thermal equilibration of hot intermediates is rapid, thus precluding most fragmentation reactions. For this reason a different mechanism is implicated for acetylene formation. We wish to report that acetylene and ethylene produced under our conditions have a C_2 precursor.

The reaction system used has been described.[6] The C_2 molecules are generated, along with C_1 and C_3, from a 16-v carbon arc under vacuum (1×10^{-4} mm). Reactions occur in condensed phase at liquid nitrogen temperature. Products were isolated by vapor phase chromatography, and their retention times and infrared and mass spectra were compared with those of known compounds.

The major products obtained when carbon vapor and methanol are deposited on a −196° surface under high dilution conditions ($CH_3OH/C_{vap} = 600$) are acetylene, ethylene, and dimethoxymethane. The latter product is simply derived from C_1.

$$2CH_3OH + C_1 \longrightarrow CH_2(OCH_3)_2$$

Two labeling experiments demonstrated that the carbon atoms of acetylene and ethylene products are derived from the electrode carbon. Carbon-14-enriched graphite electrodes[7] were used as sources of carbon vapor. The relative molar ^{14}C contents indicate two times as much ^{14}C in the acetylene and ethylene as in the dimethoxymethane (see Table I).

Table I

Product	Relative molar radioactivity[a] $^{14}C_{vap}$ + $^{12}CH_3OH$	$^{12}C_{vap}$ + $^{14}CH_3OH$	% of carbon found as product
Dimethoxymethane	1.00	2.00	14.6
Acetylene	1.90	0.14	19.2
Ethylene	1.91	0.14	1.2

[a] $(\text{Millicuries/millimole})_{C_2H_2 \text{ or } C_2H_4}/(\text{millicuries/millimole})_{\text{standard}}$.

Reaction of ^{12}C carbon vapor with ^{14}C-labeled methanol provided a complimentary result (see Table I), low relative ^{14}C content for the acetylene and ethylene. These results are best explained if C_2 is the precursor of acetylene and ethylene.

Insertion of C_1 followed by fragmentation, a favored process with "hot" carbon atoms,[4,5] is eliminated as the major source of acetylene and ethylene since one carbon atom would be derived from the electrode and the other from the methanol. The "hot" atom process may account for the deviations from whole integer relative reactivities.

Methine, CH, has been postulated as an intermediate from "hot" carbon atoms and organic substrates.[8] It is highly improbable that methine is the major pre-

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(1) P. S. Skell and R. Engel, *J. Am. Chem. Soc.*, **87**, 1135 (1965).

(2) R. Engel and P. S. Skell, *ibid.*, **87**, 4663 (1965).

(3) J. Dubrin, C. MacKay, and R. Wolfgang, *ibid.*, **86**, 4747 (1964).

(4) J. Dubrin, C. MacKay, and R. Wolfgang, *J. Chem. Phys.*, **41**, 3267 (1964).

(5) H. Ache and A. Wolf, *J. Am. Chem. Soc.*, **88**, 888 (1966).

(6) P. S. Skell, L. Wescott, Jr., J. P. Goldstein, and R. Engel, *ibid.*, **87**, 2829 (1965).

(7) Graphite electrodes were dipped into ^{14}C-labeled fructose solutions acidified with H_2SO_4, charred, and then fired at high temperature.

(8) (a) G. Stöcklin and A. P. Wolf, Proceedings of the Conference on Method of Preparing and Storing Labeled Molecules, Brussels, Euratom, 1963; (b) A. P. Wolf, *Advan. Phys. Org. Chem.*, **2**, 201 (1964); (c) A. P. Wolf and G. Stöcklin, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan 1964, p 32C; (d) J. Nichols, C. MacKay and R. Wolfgang, *J. Am. Chem. Soc.*, **88**, 1065 (1966).