substrate are due to changes in the respective activation energies. This present study confirms these findings for a series of competitive reactions involving abstraction of a primary, secondary, or tertiary hydrogen atom from a carbon atom α to an aromatic ring.

Acknowledgment. We wish to thank the Atomic Energy Commission, Division of Research, Contract No. AT(30-1)2728, for financial support of this work. We wish also to thank Dr. Böckman for checking our calculations.

The Effect of Pressure on the *cis–trans* Equilibrium in Poly-L-proline

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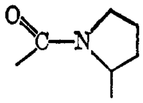
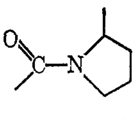
Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, and the Department of Biochemistry and Biophysics, Iowa State University, Ames, Iowa. *Received August 7, 1967*

Abstract: The effect of pressure on the equilibrium conformation of long-chain poly-L-proline has been studied by means of optical rotation measurements in the solvent acetic acid + 1-propanol (60:40 by volume). A transition from the essentially complete *trans* helix at 1 atm to the complete *cis* helix at 7000 atm was observed, with the midpoint of the transition at 2975 atm. The equilibrium transition curve obeys the equation for the one-dimensional Ising model, taking $\Delta\bar{V}/\sigma^{1/2} = -43.5$ cc/mole, where $\Delta\bar{V}$ is the standard partial molal volume change for the *trans* → *cis* reaction and σ is the interruption constant. The implications regarding the magnitude of σ are discussed, and it is concluded that σ is considerably less than unity, implying a high degree of cooperativity. Molecular models suggest that the cooperative effect originates in positive contributions to the energy of residues at junctions between *cis* and *trans* sequences.

Extensive studies[1] have shown that poly-L-proline exists in solution in two helical forms, usually designated I and II. In form I the peptide units are in the *cis* conformation.[2]



The *cis* helix is right handed and has an axial translation of 1.90 Å per residue. There are 3.3 residues per turn. In form II the peptide units are in the *trans* conformation.[3]



The *trans* helix is left handed, having 3 residues per turn, and has an axial translation of 3.12 Å per residue. The *trans* helix is thus relatively extended, while the *cis* helix is relatively compact.

It was discovered by Gornick, *et al.*,[4] that an equilibrium between the two forms exists in the solvent mixture 1-propanol–acetic acid, and that this equilibrium shifts from one form to the other within a narrow range of solvent composition. The implication of this finding is that the equilibrium is cooperative, *i.e.*, that there is a tendency for peptide units in the same state to group together along the chain. It is desirable to examine this implication in more detail to determine whether the equilibrium behaves according to a reasonable theoretical model, and to characterize the cooperativity in quantitative terms. A satisfactory theory of the dependence of a linear chain equilibrium on solvent composition is lacking at present, and one must look instead to the effects of temperature and pressure for a quantitative study.

We have been attempting to exploit pressure as an environmental variable in the study of cooperative equilibria[5] and were prompted by the above findings to undertake the present study of poly-L-proline. This seemed particularly appropriate in view of the observation of Gornick, *et al.*, that the *cis–trans* equilibrium is practically independent of temperature, implying that the enthalpy difference between the two states is essentially zero. Poly-L-proline proved to be particularly well adapted to a pressure study because the extremely slow approach to equilibrium made possible the determination of its state at high pressures by measurements of optical rotation at atmospheric pressure after removal from the pressure vessel. It was thus possible to attain higher pressures than are presently feasible in an optical rotation cell, and to observe a complete transition between the two helical forms.

Experimental Section

Materials. Poly-L-proline with a nominal molecular weight of 43,000 (DP = 440) was obtained from Mann Research Co. (Lot No. M1251). The specific rotation of this polymer when initially dissolved in acetic acid indicated that it was predominately in the *cis* form. Baker Analyzed Reagent grade acetic acid and 1-propanol were used as solvents.

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[1] Reviewed by E. Katchalski, A. Berger, and J. Kurtz, "Aspects of Protein Structure," G. N. Ramachandran, Ed., Academic Press Inc., New York, N. Y., 1963, p 205.

[2] W. Traub and U. Shmueli, *Nature*, **198**, 1165 (1963).

[3] R. M. Cowan and S. McGavin, *ibid.*, **176**, 1062 (1955).

[4] F. Gornick, L. Mandelkern, A. F. Diorio, and D. E. Roberts, *J. Am. Chem. Soc.*, 86, 2549 (1964).

[5] J. Rifkind and J. Applequist, *ibid.*, 86, 4207 (1964).

Optical Rotation. Polarimetric measurements were made with a Rudolph Model 200/S340/80AQ6 spectropolarimeter whose detection system was modified to give a reproducibility of ±0.001°, corresponding to a limit of error of ±0.3 in the specific rotation under the conditions of this study. The modifications included a John Fluke Model 412A high-voltage dc power supply for the photomultiplier tubes, a Hewlett-Packard Model 425AR dc microvoltammeter for filtering and amplifying the signal from the photomultiplier tubes, and a Hewlett-Packard 130C oscilloscope for further amplification and easy viewing of the signal. The light sources used were a Hanovia Type SH mercury lamp and a Sylvania concentrated zirconium arc lamp. Rotations were usually measured at 546, 436, and 365 mμ. Solutions were contained in 1-dm, water-jacketed polarimeter tubes which were thermostated by means of circulating water.

High-Pressure Techniques. The high-pressure apparatus was that described by Walling and Pellon.[6] The hydraulic fluid was Bayol-35, a mixture of hydrocarbons (Standard Oil Co.). Two compression pumps connected with an intensifier made possible the application of pressures up to 13,000 atm.

Poly-L-proline was dissolved in acetic acid and diluted with 1-propanol so that the solvent composition was 40% 1-propanol by volume and the polymer concentration was 0.3194 g/dl. Upon attainment of equilibrium, as indicated by the constancy of the rotation, as many as six aliquots of the solution in flexible, closed Teflon tubes were placed under pressure in the vessel described by Augurt.[7] The pressure was released at various time intervals for removal of aliquots, and the remaining tubes were immediately returned to approximately the same pressure. The rotation of the removed aliquot was measured periodically for several hours, and these measurements were extrapolated linearly to the time when the pressure was released for removal of the aliquot. The extrapolated rotation was considered to be the value characteristic of the molecular conformation present at the elevated pressure at the time the pressure was released. The observation of successive aliquots at a given pressure was continued until the extrapolated rotations remained approximately constant (generally requiring a week or more), indicating that equilibrium had been attained at that pressure.

Figure 1 shows the extrapolation of the specific rotations to the time of removal of pressure. Equilibrium had been reached at the elevated pressure for the experiments shown, with the exception of those at the two highest pressures, as noted below. It is seen that the change in rotation over the time intervals involved in these measurements is so small that the linear extrapolation to zero time presents no difficulties.

Results

The fraction f_c of peptide units in the *cis* form was obtained from the relation

$$f_c = \frac{[\alpha] - [\alpha]_t}{[\alpha]_c - [\alpha]_t} \tag{1}$$

where $[\alpha]$ is the specific rotation at some wavelength and the subscripts c and t indicate the values for the fully *cis* and fully *trans* forms, respectively. We have used the values for the latter quantities at 546 mμ reported by Gornick, *et al.*,[4] since our sample was never in one pure form in the solvent mixture used. $[\alpha]_c$ and $[\alpha]_t$ at 436 and 365 mμ were then determined by solving eq 1 simultaneously for selected sets of f_c obtained at the given wavelength. The resulting rotations are given in Table I. Subsequent determinations of f_c were thus made at the three wavelengths from the rotation data in Table II. The average of the three determinations is listed in Table II for f_c, along with the average deviations, which show that the method is fairly precise.

Table I. Specific Rotations of *cis*- and *trans*-Poly-L-prolines in Acetic Acid + 1-Propanol (60:40 by volume)

Wavelength, mμ	[α], deg cc/g dm *cis*	[α], deg cc/g dm *trans*
546	+8.0	−608.0
436	+33.7	−1060.5
365	+112.7	−1724.6

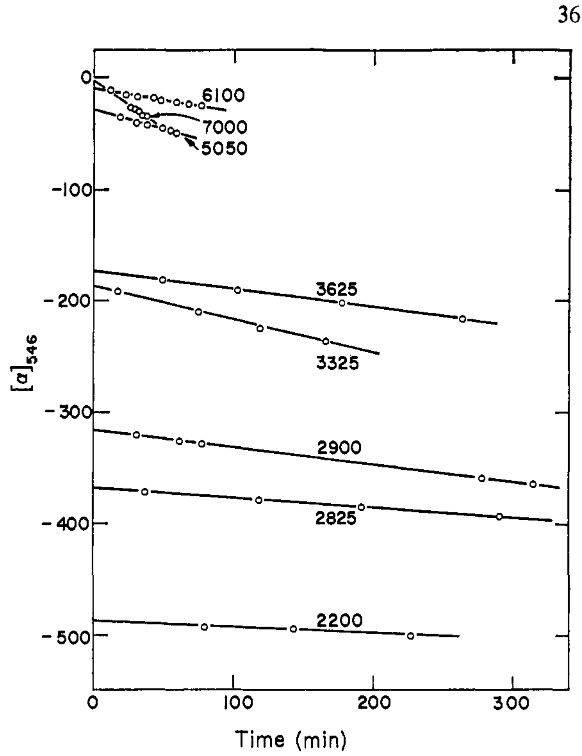

Figure 1. Specific rotation of poly-L-proline at 546 mμ in acetic acid + 1-propanol (60:40 by volume) as a function of time at 1 atm pressure after removal of elevated pressure at time zero. The elevated pressure in atmospheres is given on each experimental line.

As f_c approached unity it was found that the solutions became turbid shortly after the pressure was released, thus preventing optical rotation measurements. The rotations in parentheses in Table II correspond to this situation, and are the last nonequilibrium values determined at the stated pressure before the onset of turbidity. The values of f_c listed for these cases are halfway between the calculated nonequilibrium values and unity, as these are sufficiently accurate estimates of the equilibrium values when f_c is close to unity.

The temperature in all cases was controlled at 27–28°, with the exception of the solution at 2200 atm, where the temperature was 40°. In agreement with the earlier observation of Gornick, *et al.*,[4] that there is no significant effect of temperature on the equilibrium, the result of this experiment lies on the same transition curve as the other results (Figure 2).

To confirm the existence of true equilibrium, a sample which had reached equilibrium at 7000 atm was allowed to reach a new steady rotation at 3325 atm. The resulting f_c is seen in Figure 2 to lie on the same curve as all the other values, demonstrating that the same state is approached from either direction at a given pressure. This result also shows that no irreversible process has occurred at 7000 atm, such as might have been used to account for the onset of turbidity on release of high pressure noted above.

Discussion

Poly-L-proline is a linear polymer in which each peptide unit[8] can be in one of two states (*cis* or *trans*).

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[6] C. Walling and J. Pellon, *J. Am. Chem. Soc.*, 79, 4776, 4786 (1957).

[7] T. Augurt, Ph.D. Thesis, Columbia University, 1965.

Table II. Specific Rotations of Poly-L-proline in Acetic Acid + 1-Propanol (60:40 by volume) as a Function of Pressure

Pressure, atm	[α], deg cc/g dm 546 mμ	436 mμ	365 mμ	f_c
1	−569.5	−992.2	−1609.7	0.063 ± 0.0005
2200	−486.7	−824.2	−1327.6	0.210 ± 0.009
2825	−369.1	−641.2	−1023.2	0.382 ± 0.001
2900	−316.5	−532.9	−846.3	0.478 ± 0.004
3325	−186.1	−331.2	−496.1	0.672 ± 0.005
3625	−173.3	−279.0	−428.5	0.708 ± 0.004
5050	−27.6	−26.3		0.944 ± 0.002
6100	(−6.4)			0.988 ± 0.012
7000	(−4.1)			0.990 ± 0.010

Moreover, it is reasonable to suppose that the free energy of a given state of a peptide unit depends on the interactions of that unit with only a small number of neighbor units. Therefore, the one-dimensional Ising model,[9] which is a fairly good representation of one-stranded helix–coil equilibria,[10–12] should be applicable to the *cis–trans* equilibrium in poly-L-proline.

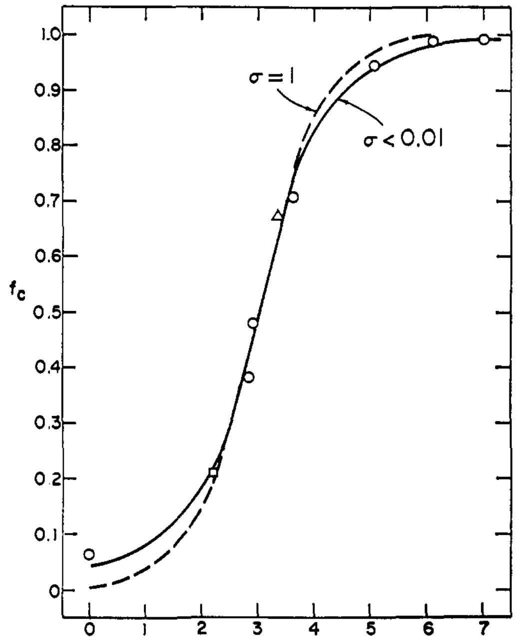

Figure 2. Fraction of peptide units in the *cis* form as a function of pressure for poly-L-proline in acetic acid + 1-propanol (60:40 by volume): (○) equilibrium approached from low f_c at 28°, (△) equilibrium approached from high f_c at 28°, (□) equilibrium approached from low f_c at 40°. The curves are calculated from eq 2 (see text).

By one accepted definition, the Ising model takes into account only nearest neighbor interactions. For systems with further neighbor interactions of short range, such as the α-helical polypeptides, the mathematical results for the simple Ising model are still a good approximation if there is a high degree of cooperativity.[10,11] As will be shown below, this condition is most likely met in poly-L-proline. Thus it is reasonable to expect that the pressure transition curve would be represented by the equation for the infinitely long Ising model,[11] namely

$$f_c = \frac{1}{2} + \frac{s - 1}{2[(1 - s)^2 + 4\sigma s]^{1/2}} \qquad (2)$$

where f_c is the fraction of residues in the *cis* form; the stability constant s is the equilibrium constant for the conversion of a residue from *trans* to *cis* at the end of a *cis* sequence in the molecule; the interruption constant σ is the equilibrium constant for a process in which a molecule containing ν *cis* sequences is converted to a molecule containing $\nu + 1$ *cis* sequences, keeping the number of *cis* peptide units in the molecule fixed.

The dependence of s upon pressure P is governed by

$$(\partial \ln s/\partial P)_T = -(\Delta \bar{V}/RT) \qquad (3)$$

where T is the absolute temperature, R is the gas constant, and $\Delta \bar{V}$ is the change in partial residue-molal volume for the conversion from *trans* to *cis* at infinite dilution. From eq 2 and 3 it follows that the slope of the pressure transition curve at the midpoint is

$$(\partial f_c/\partial P)_T = -(\Delta \bar{V}/4RT\sigma^{1/2}) \qquad (4)$$

From the experimental data one thus finds $\Delta \bar{V}/\sigma^{1/2} = -43.5$ cc/mol. Assuming that this quantity is constant throughout the transition, one calculates the transition curves shown in Figure 2 from eq 2 and 3. In this calculation the values of $\Delta \bar{V}$ and σ are needed separately, but one of these can be set arbitrarily. If one chooses $\sigma < 0.01$, then the calculated curve does not depend noticeably on the value chosen[13] and is governed solely by the ratio $\Delta \bar{V}/\sigma^{1/2}$.

The question naturally arises as to whether these observations confirm the existence of a cooperative phenomenon, and whether any information can be gained as to the magnitude of the cooperativity. If the system were noncooperative we would have $\sigma = 1$, and hence $\Delta \bar{V} = -43.5$ cc/mol. This figure would then imply that the effective volume of a residue is reduced by an amount comparable to its molal volume (approxi-

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[8] The terminology for polypeptide structures used in this discussion is that recommended by J. T. Edsall, P. J. Flory, J. C. Kendrew, A. M. Liquori, G. Nemethy, G. N. Ramachandran, and H. A. Scheraga, *Biopolymers*, **4**, 121 (1966).

[9] E. Ising, *Z. Physik*, 31, 253 (1925).

[10] B. H. Zimm and J. K. Bragg, *J. Chem. Phys.*, **31**, 526 (1959).

[11] J. Applequist, *ibid.*, **38**, 934 (1963).

[12] J. Applequist and V. Damle, *J. Am. Chem. Soc.*, **88**, 3895 (1966).

[13] A simple proof of this follows. When $\sigma \ll 1$, the entire transition takes place under conditions where $s \cong 1$. Then eq 2 can be rearranged in the form

$$f_c = \frac{1}{2} + \frac{(s - 1)/\sigma^{1/2}}{2[(s - 1)^2/\sigma + 4]^{1/2}} \qquad (5)$$

Also, eq 3 can be integrated to give

$$s - 1 \cong \ln s = -(\Delta \bar{V}/RT)(P - P_c) \qquad (6)$$

where P_c is the pressure at which $s = 1$. By substituting eq 6 into eq 5, one finds that f_c is a function of $\Delta \bar{V}/\sigma^{1/2}$ as required.

mately 70 cc/mol[14]) on conversion from *trans* to *cis*. The known factors which could cause such a drastic decrease in volume for a reaction in solution are the formation of new covalent bonds, the formation of ions, or the exposure of large, previously inaccessible voids to solvent molecules.[15] However, none of these effects is consistent with our present understanding of the process occurring in poly-L-proline, namely, a rotation about the C′–N bond. Since one may reasonably expect a relatively small volume change for this process, the observed value, $\Delta \bar{V}/\sigma^{1/2} = -43.5$ cc/mol, suggests that σ is likewise small and that a cooperative effect is present.

The *cis–trans* isomerizations in olefins present what may be regarded as a rough analogy to the poly-L-proline case. The known volume changes for olefins are in the vicinity of -2 cc/mol[16] (using the same sign convention as for poly-L-proline), thus supporting the notion that $\Delta \bar{V}$ for poly-L-proline should be small. A $\Delta \bar{V}$ value of about -2 cc/mol would imply a σ value of about 0.003, though these numbers can only be regarded as illustrative, since the analogy to the olefins is not a precise one. The fact that the experimental data in Figure 2 show the better fit to the curve calculated for $\sigma < 0.01$ is at least consistent with this estimate, but this criterion is obviously not sensitive enough to be conclusive.

Engel[17] has recently reported a study of the *cis–trans* isomerization of poly-L-proline brought about by variation of solvent composition in a mixture of 1-butanol and benzyl alcohol. He estimates $\sigma \cong 10^{-5}$ from the molecular weight dependence of the relaxation time for restoration of equilibrium after introducing small perturbations of the equilibrium. To be consistent with our findings, this would require that $\Delta \bar{V} \cong -0.1$ cc/residue mol, assuming that the difference in solvent has no effect. Engel's estimate from kinetic data is, however, based on the additional assumptions of the Schwarz theory,[18] and it is worth considering that a test of these assumptions would be found in a comparison of accurate values of σ obtained from equilibrium and kinetic data. The piece of missing information needed for determination of an "equilibrium" σ from our data is, of course, the precise value of $\Delta \bar{V}$. (A direct determination of this quantity may be possible; however, our own efforts to carry out the measurement in a sensitive dilatometer failed because an otherwise undetected instability of the solvent mixture resulted in volume changes greater than that due to the *cis–trans* isomerization for dilute solutions of the polymer.)

To gain some insight into possible origins of the cooperative effect in poly-L-proline, we have examined Courtauld space-filling models.[19] The models reveal at least some of the interactions which are likely to contribute to the junction free energy ΔF_σ, which is equal to $-RT \ln \sigma$, and is the free energy of formation of a pair of successive junctions between *cis* and *trans* residues. We note particularly the following observations.

(i) When a *cis* sequence follows a *trans* sequence in proceeding from the amino to the carboxy terminus, extensive overlap of atoms occurs near the junction. While the strain produced can be relieved to a considerable extent by rotation of the C^α–C' bonds closest to the junction out of their normal potential energy minima, the calculations of de Santis, *et al.*,[20] indicate that this minimum is a rather sharp one, so that large energies are required for the rotation. Thus it appears that a substantial positive energy is associated with such a junction. Where a *trans* sequence follows a *cis* sequence, steric effects do not appear to be as important.

(ii) The compactness of the *cis* helix presents opportunities for attractive interactions between atoms in adjacent turns of the helix. In particular, hydrogens on C_i^α and C_i^β are located at approximately the distance necessary for a van der Waals contact with O_{i+3}.[8] It is reasonable to suppose that an attractive interaction between these atoms is important in stabilizing the *cis* helix. Thus, the three residues for which this interaction is missing at one end of the helix will have a positive energy associated with them. The importance of this contribution will depend to some extent on the structure of the junction region, since the missing interactions can be partially compensated for by attractive van der Waals interactions between *cis* and *trans* peptide units at the junction.

(iii) The openness of the *trans* helix suggests that interactions with solvent help to stabilize it. This is consistent with the observation that the *trans* helix is the more stable one in strongly hydrogen bonding solvents.[1] The steric interactions at the junctions mentioned under (i) are such as to reduce the accessibility of solvent to *trans* peptide units located near a junction, very likely resulting in a positive contribution to the free energy of the *trans* units.

The contributions to ΔF_σ cited here are largely, if not entirely, energetic in origin. A cooperative effect of this type would contrast with that found in α-helical polypeptides, where the effect is believed to be largely entropic in origin.[10,11]

Some further discussion of intramolecular interactions in poly-L-proline has been given by Schimmel and Flory.[21]

In summary, the present study has shown that the behavior of the *cis–trans* equilibrium in long-chain poly-L-proline as a function of pressure can be satisfactorily interpreted in terms of the one-dimensional Ising model, insofar as the available data permit a comparison between experiment and theory. A quantitative characterization of the equilibrium has been obtained in the quantity $\Delta \bar{V}/\sigma^{1/2} = -43.4$ cc/mol which is so large as to represent a significant cooperative effect. An examination of molecular models has suggested that the cooperative effect arises primarily from positive energy contributions at the junctions between *cis* and *trans* peptide units in a molecule.

Acknowledgments. This investigation was carried out at Columbia University with research grant support from the National Institute of General Medical Sciences

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[14] E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids, and Peptides," Reinhold Publishing Corp., New York, N. Y., 1943, p 372.

[15] S. D. Hamann, "High Pressure Physics and Chemistry," Vol. 2, R. S. Bradley, Ed., Academic Press Inc., New York, N. Y., 1963, p 138 ff.

[16] Reference 15, p 139.

[17] J. Engel, *Biopolymers*, 4, 945 (1966).

[18] G. Schwarz, *J. Mol. Biol.*, 11, 64 (1965).

[19] Obtained from Ealing Corp., Cambridge, Mass.

[20] P. de Santis, E. Giglio, A. M. Liquori, and A. Ripamonti, *Nature*, **206**, 456 (1965).

[21] P. R. Schimmel and P. J. Flory, *Proc. Natl. Acad. Sci. U. S.*, **58**, 52 (1967).

(GM-10882) and predoctoral fellowship support to J. M. R. from the National Science Foundation and the National Institutes of Health. We are grateful to Professor Cheves Walling for making his high-pressure apparatus available to us and to Dr. Thomas Augurt for his assistance in its use.

Photochromic Fulgides. Spectroscopy and Mechanism of Photoreactions

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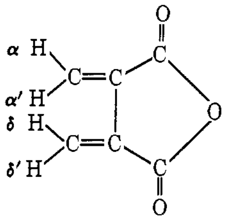
Abstract: The photochromism of a number of fulgides has been studied, and the process has been shown to be a molecular phenomenon. The primary photochemical step is a photobridging process which accounts for the formation of a cyclic colored structure. Proof for the nature of the photocolored species is inferred from a subsequent reaction. Substitution has an effect on the relative concentration of the colored form at the photostationary state and is discussed. Fluorescence exists in some cases but no phosphorescence can be observed. Thermal and photoerasure of the colored form is possible.

The fulgides may be obtained by substitution of the lettered hydrogen positions in dimethylenesuccinic anhydride.



When one of the hydrogens is substituted by an aryl group, the crystals have initially a yellow to reddish shade. The effect of light is to deepen the color. Stobbe[2] first made a crystallographic and spectroscopic investigation and came to the conclusion that the photochromism of these substances was exclusively a crystalline phenomenon. Further, no identification of the nature of the colored species has ever been cited despite continued study by Hanel.[3]

All known photochromic fulgides contain a phenyl group. Also, 1-phenylnaphthalene-2,3-dicarboxylic acid anhydride was isolated on prolonged irradiation at room temperature of an iodine-containing solution of dibenzylidenesuccinic anhydride.[4,5] Also, 1,4-diphenyl-1,3-butadiene undergoes photochemical reaction to 1-phenylnaphthalene.[6]

We anticipated that the photochromic behavior of the fulgides was a molecular phenomenon. Therefore, as a part of our continuing investigation to evaluate various spectroscopic parameters of molecules and their importance in photochemistry, we have investigated the spectroscopic and photochemical behavior of a number of fulgides. The purpose of the present study is (1) to elucidate the nature and mechanism of production of the colored species, (2) to correlate the low-temperature absorption and emission characteristics with the photochemical behavior, and (3) to determine the effect of the nature of substitution on the photochemical and spectroscopic properties of the fulgides.

Experimental Section

In general, the syntheses followed those described in earlier work.[1] The itaconic esters (methylenesuccinic acid ethyl ester) were prepared by a modified Stobbe condensation of Johnson, *et al.*[7] Further condensation of the itaconic ester with an appropriate aldehyde or ketone using sodium ethoxide yielded the corresponding substituted dimethylenesuccinic acid monoester. Hydrolysis in ethanolic potassium hydroxide solution gave the fulgenic acid (dimethylenesuccinic acid). This, in turn, was converted to the anhydride form by refluxing in an acetyl chloride solution. The anhydrides were purified by recrystallization in a variety of solvents depending on the solubility properties of the particular fulgide and also by chromatography on a neutral silica gel column. Purity was determined by thin layer chromatographic analysis as well as by melting point determination.

The low-temperature absorption measurements were obtained on a Cary Model 15 spectrophotometer using 2.0-mm rectangular quartz cells immersed in an optical dewar filled with liquid nitrogen. In every instance, 2-methyltetrahydrofuran (2MeTHF) was used as the solvent for both absorption and emission spectra. The 2MeTHF was purified by refluxing over lithium aluminum hydride and passage through an activated alumina column.

The emission set up consisted of a 1-kW xenon source, an exciting monochromator, and an analyzing monochromator with an EMI 9558 B photomultiplier. In all cases, the emission recorded was that from the front surface of the sample cell. A 150-W tungsten lamp with a built-in parabolic reflector was used to obtain the excitation spectra in the 400–500-mμ region. Some of the excitation spectra were corrected for the decrease in intensity of the source and for the change in efficiency of the exciting monochromator as a function of wavelength. For the same cases, the relative quantum efficiency of emission was also calculated. The emission spectra were not corrected for photomultiplier tube response as a function of wavelength.

The relative quantum yields of emission were calculated as follows

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(1) Taken from a thesis submitted in partial fulfillment for the M.S. degree.

(2) H. Stobbe, *Ann.*, 380, 1 (1911).

(3) L. Hanel, *Naturwissenschaften*, 37, 91 (1950).

(4) H. Stobbe, *Ber.*, 40, 3372 (1907).

(5) A. El-Abbady and L. El-Assal, *J. Chem. Soc*, 1016 (1959).

(6) G. J. Fonken, *Chem. Ind.* (London), 1327 (1962).

(7) W. Johnson, J. Peterson, and W. Schneider, *J. Am. Chem. Soc.*, 69, 74 (1947).