TABLE I

DISPERSION CONSTANTS FOR PHTHALIMIDES OF (−)(S) α-PHENYLETHYLAMINES (CHLOROFORM SOLUTION)

$$[M] = -\frac{A}{\lambda^2 - x} + \frac{B}{\lambda_1 - y}$$

| Z	A	x (μ^2)	B	y (μ^2)	$[M]_D$	λ (mμ)	Trough $[M]$	λ (mμ)	Peak $[M]$
NO₂	111	0.085	38	0.104	−267	365	−995	335	−150
H	85	.070	30	.104	−180	400	−410	340	+190
Cl	114	.070	38	.104	−253	390	−590	340	+200
Br	114	.070	38	.104	−255	390	−600	340	+170
I	117	.070	38	.104	−275	390	−640	340	+100
OCH₃	125	.070	50	.104	−250	400	−510	350	+ 50
NH₂	186	.075	100	.104	−245	425	−450	380	−290

These compounds were prepared from the phthalimide of optically pure (−)S)α-phenylethylamine via nitration, reduction and diazotization; they gave correct analyses. The Drude constants are presented only as a concise means of summarizing the dispersion curves and do not represent unique solutions of the two-term equations. The constants for the positive term are the more reliable since measurements could be made to the beginning of the positive Cotton effect. All rotations were measured using a manual Rudolph spectrophotopolarimeter (see ref. 1, pp. 18–26) purchased with funds from the Indiana Elks, the American Cancer Society, the National Institute of Health and the Research Corporation.

the elaborate computations needed for the determination of "reduced rotational strengths."[2]

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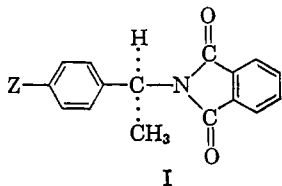
The phthalimide group has one plane of symmetry containing the atoms and sigma bonds (the σ plane) and another bisecting both rings and lying parallel to the pi orbitals (the π plane). In a particular conformation atoms which are

II   III
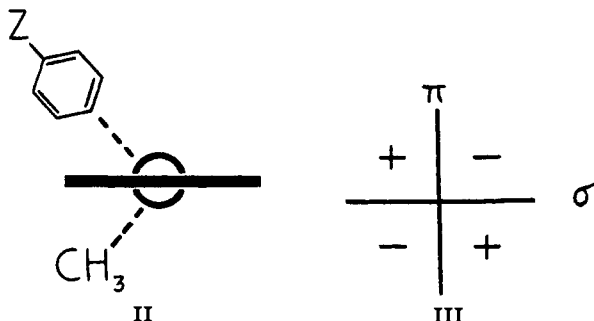
distributed asymmetrically among the quadrants defined by those planes could produce a dissymmetric perturbation of an electronic transition of the phthalimido group and so cause a Cotton effect at the absorption band corresponding to that transition.[3,4,5] We assume, tentatively, that the sign of the contribution of an atom or group to the phthalimido Cotton effect of a particular conformation is determined simply by the quadrant in which it lies. The observed Cotton effect will be a summation of those of the individual conformations; it is necessary (but not sufficient) that certain conformations be more abundant than others for any Cotton effect to be observed at all. Models

indicate that the oxygen atoms would produce severe steric stress in certain conformations and that, in the present series of compounds, only the conformation shown in II[6] will be reasonably free of such stress. It thus appears that atoms in the quadrant occupied by the phenyl group in II make positive contributions to this Cotton effect; signs may be given to the other quadrants on the basis of their symmetry relationships to this one (III). It is at least an interesting coincidence that the same σ-π plane diagram (III) can be used for predicting ketonic Cotton effect by use of the Octant Rule.[4]

(6) The horizontal bar represents the π plane of the phthalimido group projecting forward from the asymmetric carbon atom.

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OPTICAL ROTATORY DISPERSION STUDIES. XLIII.[1]
ABSOLUTE CONFIGURATIONAL ASSIGNMENT OF
α-SUBSTITUTED CARBOXYLIC ACIDS BY
ANOMALOUS ROTATORY DISPERSION OF THEIR
ACYLTHIOUREA DERIVATIVES[2]

Sir:

Our recent investigations[3] have amply demonstrated the utility of anomalous rotatory dispersion measurements for the solution of a variety of organic chemical problems. As Cotton effect curves are only shown by substances containing an optically active chromophore (e.g., carbonyl group) with suitable spectral characteristics (usually low intensity maximal absorption in an accessible spectral range), there are a number of important classes of organic compounds (e.g., alcohols, amines, carboxylic acids) that do not lend themselves to this anomalous rotatory dispersion approach because of their unsuitable spectral properties. In order to circumvent this problem, we have been searching for easily prepared derivatives which absorb in the near ultraviolet or visible

(2) Ref. 1, pp. 150–177 (Chapter by A. Moscowitz).

(3) This analysis is parallel to one used in a theoretical treatment of ketonic Cotton effects.[3]

(4) See ref. 1, pp. 178–190.

(5) The question of whether there is a third plane cutting each of these quadrants into two octants is, for the present, academic and will be left open.

(1) Paper XLII, C. Djerassi, A. Fregda and B. Sjöberg, in press.

(2) Supported by grant No. CRTY-5061 from the National Cancer Institute, National Institutes of Health, U. S. Public Health Service, and by the National Science Foundation.

(3) For a detailed summary see C. Djerassi, "Optical Rotatory Dispersion: Applications to Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.
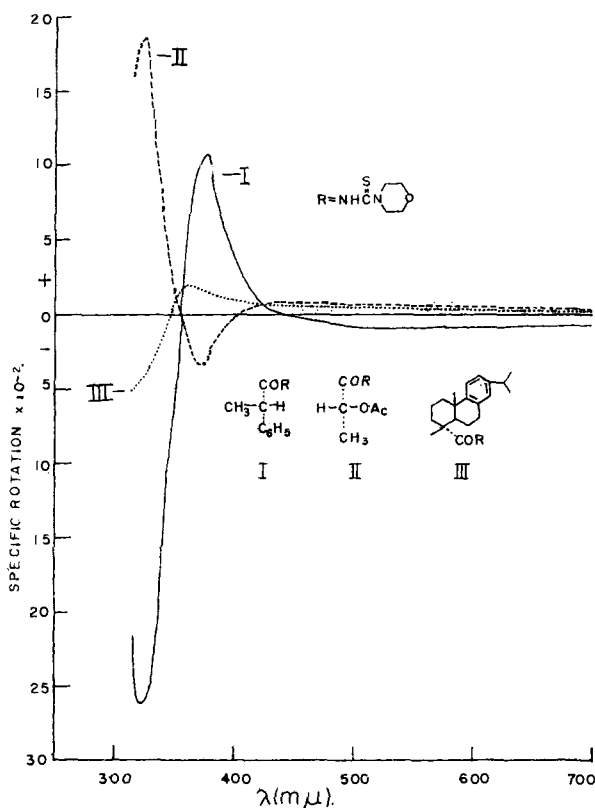
Fig. 1.

portion of the spectrum. Thus dithiocarbamates and xanthates of α-amino and α-hydroxy acids, respectively, have lent themselves admirably to this approach[4] and we now wish to record a satisfactory solution to the problem of converting a carboxyl group into a "chromophoric" derivative[5] exhibiting a Cotton effect.

After an extensive search, we have found acyl-thioureas (RCONHC(=S)NR′₂), notably of morpholine (acyl morpholinothiocarbamides), to be the most desirable derivatives because of their ease of preparation (treatment of acid chloride with potassium thiocyanate and then morpholine) and their low intensity ultraviolet absorption maximum near 340 mμ, which is "optically active." Most importantly, *the resulting Cotton effect curves apparently can be used for absolute configurational assignments of the α-asymmetric center, members of the L-series exhibiting a positive Cotton effect and of the D-series, a negative one.* Typical curves are shown in Fig. 1.

The nature of the α-substituent does not appear to be critical: the morpholinothiocarbamides of L-(−)-hydratropic acid (I) and L-(+)-α-methyl-butyric acid show positive Cotton effects, while negative ones are associated with the corresponding derivatives of D-(−)-acetoxylactic acid (II) and D-(+)-α-(2-naphthyl)-propionic acid. It

(4) B. Sjöberg, A. Fredga and C. Djerassi, THIS JOURNAL, 81, 5002 (1959).

(5) One possible derivative is the methyl ketone available by the reaction of methyl lithium with a carboxylic acid. Rotatory dispersion curves of such ketones already have been examined by C. Djerassi and L. E. Geller, ibid., 81, 2789 (1959), and by B. Sjöberg, Arkiv Kemi, 15, 473 (1960).

should be noted that the confusion associated with opposite sign rotations at the sodium D-line by members of the same series is eliminated when the Cotton effects of acyl thioureas are considered.

The presently described approach also may prove useful in the diterpene field for configurational assignments of the carboxyl group, since dehydro-abietyl morpholinothiocarbamide (III) shows a positive Cotton effect (Fig. 1), in contrast to the negative one exhibited by acetoxypodocarpyl morpholinothiocarbamide. The only stereochemical difference between these two resin acid derivatives resides in the asymmetric center adjacent to the carboxyl group.

As an example of a typical preparation, 120 mg. of dehydroabietic acid was heated for two hours with 2.5 cc. of thionyl chloride, excess reagent was removed, the residual acid chloride was dissolved in 2 cc. of anhydrous acetone and 44 mg. of freshly dried potassium thiocyanate in 2 cc. of acetone was added. After heating under reflux for one hour, 0.6 cc. of morpholine was added, heating continued for ten minutes and the mixture let stand overnight. Removal of the solvent, addition of water and dilute acid, followed by ether extraction afforded 86% of III, m.p. 102–104° (from hexane), λ_{max}^{MeOH} 282 and 340 mμ, log ε 4.16 and 2.41.

Rotatory dispersion curves of additional acid derivatives and further details of this approach will be discussed in detail in our complete paper.[6]

(6) We are indebted to Mrs. Ruth Records for the rotatory dispersion measurements.

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SYNTHESIS OF TRIPHOSPHONITRILIC DIAMIDETETRAAZIDE

Sir:

As part of a study involving the synthesis and the chemical and physical properties of phos-phonitrilic chloride and cyanuric chloride derivatives we wish to report the preparation and isolation of a mixed triphosphonitrilic amidoazido derivative, $P_3N_3(NH_2)_2(N_3)_4$, which to our knowledge is the first crystalline azide of the phosphonitrilic system to be synthesized. The triphosphonitrilic hexa-azide was prepared by Grundmann and Rätz[1] and reported to be an unstable oil. Related tri-phosphonitrilic derivatives which have been reported by other investigators as solid products are the hexahydrazide,[2] $P_3N_3(N_2H_3)_6$; the hexathio-cyanate,[3] $P_3N_3(CNS)_6$; the hexaamide,[4] P_3N_3-$(NH_2)_6$; and the tetraanilidediamide,[5] $P_3N_3(NH$-$C_6H_5)_4(NH_2)_2$.

The triphosphonitrilic diamidetetrachloride starting material was obtained readily by the reaction of an ether solution of $P_3N_3Cl_6$ with aqueous am-

(1) C. Grundmann and R. Rätz, Z. Naturforsch., 10b, 116 (1955).

(2) R. J. A. Otto and L. F. Audrieth, THIS JOURNAL, 80, 3575 (1958).

(3) G. Tesi, R. J. A. Otto, F. G. Sherif and L. F. Audrieth, ibid., 82, 528 (1960).

(4) L. F. Audrieth, R. Steinman and A. D. F. Toy, Chem. Revs., 32, 109 (1943).

(5) H. Bode, K. Butow and G. Lienau, Chem. Ber., 81, 547 (1948).