

Chiroptical Properties and Molecular Geometry of Substituted Succinic Anhydrides and Imides

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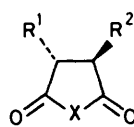
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U.v. and c.d. spectra have been measured for several α -substituted succinic anhydrides and imides. The observed Cotton effect signs corresponding to the two $n-\pi^*$ electronic transitions can be explained with the octant rule. The strong substituent and solvent dependence of the spectra is a result of the equilibrium between two skewed conformers of the five-membered ring. The geometry and relative energies of the conformers were found from the molecular mechanics (MM2) calculations.

It has been suggested that the carboxylic anhydrides and imides of the same stereochemical type should exhibit similar c.d. curves.¹ This expectation is justified by the same symmetry, isoelectronic structure, and analogous character of electronic transitions of these chromophores which show two $n-\pi^*$ bands in the 250—220 nm region.¹⁻³ The chiroptical properties of cyclic anhydrides have been a subject of recent interest^{2,3} and two rules for correlation of the Cotton effect (C.e.) sign with the molecular geometry of these compounds have been suggested. Snatzke *et al.*² have proposed the 12-sector rule for the planar (C_{2v}) and the helicity rule for the skewed (C_2) anhydride chromophores. Sjöberg and Obenius³ have studied c.d. spectra of alkyl substituted succinic anhydrides and observed that the C.e. magnitude and sign are very sensitive to changes in solvent, temperature, and substituent size. They have stated that the c.d. sign of these compounds can hardly be rationalized by the 12-sector rule. Although the c.d. spectra have been reported for some imides,⁴⁻⁷ there has been no systematic investigation of this chromophore. However, imides are better suited models than anhydrides for the study of solvent effects and for spectroscopic assignments because of better separation of the $n-\pi^*$ absorption bands.

The aim of the present study is to examine the chiroptical properties of a relatively broad class of cyclic anhydrides and imides. The u.v. and c.d. spectra were measured in different solvents and a new sector rule is proposed for stereochemical correlations. The c.d. behaviour of the compounds studied is discussed in terms of the ring geometries derived from molecular mechanics calculations. This paper deals with the five-membered ring compounds of C_2 or C_{2v} local symmetry of the chromophores^{2,3} and the subsequent paper is devoted to the six-membered ring compounds with a more complicated symmetry.^{8,9} Some α -alkyl and α -hetero substituted succinic anhydrides and imides (1)—(12) of known absolute configuration have been synthesized and their spectra studied.

Molecular Geometry.—Since the analysis of c.d. spectra is assisted by a clear picture of molecular geometry and because experimental data of the structure are known only for a few anhydrides and imides, molecular mechanics (MM) calculations were performed for some anhydrides. The MM method has been shown to be a very reliable and efficient way of determining conformations and energies for a wide variety of compounds.¹⁰ Recently, this technique has been successfully applied to the interpretation of the c.d. spectra of ketones.¹¹ The attempt to extend the original Allinger's MM2 force field¹² to anhydrides has been reported,¹³ however, this extension is limited to the five-membered rings and our efforts to apply this parameterization to the six-membered rings and acyclic compounds failed. For this reason a new parameterization derived from MNDO¹⁴ calculations is proposed (Appendix). The computed geometries



(1a) $R^1 = H, R^2 = Me, X = O$

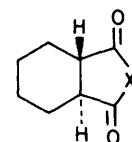
(1b) $R^1 = H, R^2 = Me, X = NH$

(2a) $R^1 = R^2 = Me, X = O$

(2b) $R^1 = R^2 = Me, X = NH$

(11) $R^1 = R^2 = OH, X = NH$

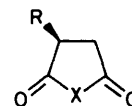
(12) $R^1 = R^2 = OBU^t, X = NH$



(5a) $X = O$

(5b) $X = NH$

(5c) $X = NMe$



(3a) $R = BU^t, X = O$

(3b) $R = BU^t, X = NH$

(4a) $R = Ph, X = O$

(4b) $R = Ph, X = NH$

(6) $R = OH, X = NH$

(7a) $R = OMe, X = O$

(7b) $R = OMe, X = NH$

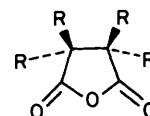
(8a) $R = OBU^t, X = O$

(8b) $R = OBU^t, X = NH$

(9) $R = ^+NH_3, X = NH$

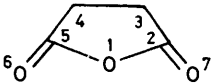
(10) $R = NHCO_2CH_2Ph, X = NH$

of different type model compounds agree well with the experimental data. The calculations are restricted to anhydrides and the geometry of imides is expected to be similar to that of corresponding anhydrides; the possible differences should be deduced from the spectra. The results (selected torsional angles) are presented in Table 1. The succinic anhydride skeleton (13) is shown to be almost planar in agreement with the crystal



(13) $R = H$

(14) $R = Me$

Table 1. Selection torsion (O) angles of succinic anhydrides calculated from MM2


Compound	(1-2-3-4)	(1-5-4-3)	(3-2-1-5)	(2-1-5-4)	(2-1-5-6)	(5-1-2-7)	(2-3-4-5)	(1-2-3-X) ^d
(1a)	-17.3	-15.9	5.4	7.9	-174.6	-169.6	19.3	-141.5
(2a)	-18.5	-18.5	7.4	7.4	-170.1	-170.1	21.4	-142.4
(3a)-eq ^b	17.3	16.7	-6.1	-7.5	174.0	171.0	-19.7	146.0
(3a)-ax ^b	-14.5	-12.7	3.8	7.1	-176.0	-172.1	15.7	111.4
(4a)	4.7	14.2	-11.8	4.1	168.9	-177.2	-10.9	134.3
(5a)	30.1	30.1	-12.1	-12.1	165.3	165.3	-35.0	151.5
(7a)-eq ^c	10.6	11.9	-5.5	-3.5	174.3	178.2	-13.0	131.5
(7a)-ax ^c	-17.6	-16.1	5.3	8.2	-175.3	-170.6	19.5	98.8
(13)	-0.5	-0.5	0.2	0.2	-179.8	-179.8	0.6	-119.5
(14)	-24.1	-24.1	9.7	9.7	-167.7	-167.7	27.7	-94.9
(14) ^d	(-26.5 ± 1.3)		(10.8 ± 0.6)				(30.4 ± 1.6)	

^a X, α -Substituent. ^b The calculated energy of the equatorial (eq) form is 4.1 kJ mol⁻¹ lower than the axial (ax) one. ^c The calculated energy of the axial (ax) form is 6.0 kJ mol⁻¹ lower than the equatorial (eq) one. ^d The experimental values²³ in parentheses.

structure.¹⁵ The small deviation from planarity of (13), *ca.* 4° ($\pm 2^\circ$) shown by electron diffraction in the gas phase results from large out-of-plane vibrations.¹⁶ Analogously, succinimide has planar geometry in the solid state.¹⁷ The MM2 calculations for α -substituted succinic anhydrides reveal that the substitution causes distortion of the ring from planarity, however, the anhydride moiety is only slightly skewed. The conformation with the α -substituent in the equatorial (pseudoequatorial) position is preferred for compounds (1a)–(4a) whereas the α -methoxy group in (7a) prefers the axial position. The MM2 method indicates two energy minima (axial and equatorial conformers for only two compounds, (3a) and (7a). However, the calculations are performed for isolated molecules (in the gas phase) and neglect solvation which is an important factor. Owing to this effect, it is expected that, in solution, there is a conformational equilibrium between at least two conformers for most of the compounds studied. This supposition is confirmed by the strong solvent and temperature dependence of the c.d. spectra. The X-ray structures known for some substituted succinic anhydrides and imides,^{18–22} confirm the influence of substituents on the ring conformation: anhydrides are generally skewed¹⁹ and imides show various types of ring geometries, from planar to considerably deviated from planarity. Evidently, crystal packing influences the ring conformation since even closely related species may differ in geometry; *e.g.* α -phenylsuccinimide (4b) is nearly planar²¹ whereas α -(3-bromo-4-ethoxyphenyl)succinimide is significantly distorted from planarity.²² Several substituents cause stronger effects and thus tetramethylsuccinic anhydride (14) is considerably skewed in the gas phase²³ in agreement with the MM2 result (a similar geometry has been reported for *N*-phenyltetramethylsuccinimide in the crystal state).²⁴ Bicyclic derivatives (5a) and (5b) occupy an extreme position; they exhibit strong twisting not only of the five-membered rings but also the chromophores as shown by the MM2 result for (5a) and the X-ray structure of imide (5b).²⁰

U.v. Spectra.—The u.v. spectra of imides exhibit two bands of moderate intensity at 250 and 220 nm and strong absorption near 190 nm,²⁵ *e.g.* succinimide shows λ_{max} at 242.5 (ϵ 77) and 217.5 nm (ϵ 152) in methanol, and λ_{max} 193 nm (ϵ 18 800) in water. Most of the spectra exhibit vibronic fine structure which is more pronounced in the 220 nm band. Although it is almost impossible to distinguish between the two bands near 225 nm

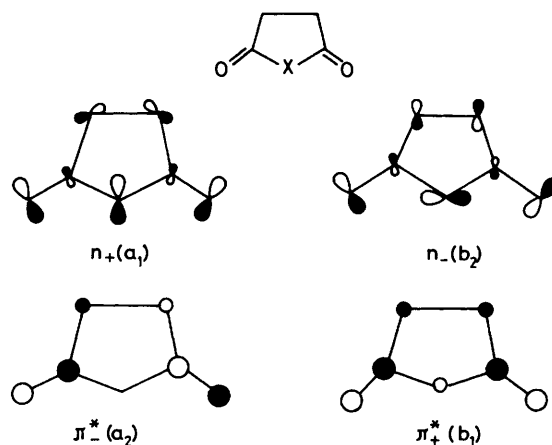


Figure 1. Qualitative representation of the highest occupied and lowest unoccupied anhydride and imide MOs (π MOs are viewed along axis of the p_z orbitals)

for succinic anhydrides it is quite easy for the six-membered ring anhydrides.⁸ The assignment of the two lowest energy electronic transitions was based on the CNDO/2-CI calculations performed for the planar succinic anhydride and succinimide molecules.[†] The shape of the molecular orbitals (MO) (Figure 1) involved in these excitations is essentially the same for anhydrides and imides, and is very similar to other β -dicarbonyl compounds.^{26,27} The energetic order of the MOs is $\pi^* > \pi^* > n_- > n_+$. The two highest occupied MOs n_+ and n_- result from through-bond interaction of carbonyl oxygen p -orbitals and are considerably mixed with skeletal σ -orbitals. The n_+/n_- splitting is of the order of 0.8 eV for anhydrides and 0.7 eV for imides as is known from photoelectron spectroscopy.²⁷ The two lowest-energy transitions are both of $n-\pi^*$ character; the first $A_1 \rightarrow B_1$ is an admixture of $n_+-\pi^*$ and $n_--\pi^*$, and the second, $A_1 \rightarrow$

[†] The calculations were performed for the geometries derived from X-ray structure determinations.^{15,17} The standard parameterization (J. A. Pople and D. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970, ch. 3.5) was used and CI procedure was limited to 27 singly excited configurations.

Table 2. C.d. data of substituted succinic anhydrides and imides (λ in nm; $[\theta]$ in $^{\circ}$ cm² dmol⁻¹)

Compd.	Solv. ^a	$\lambda(10^{-3} [\theta])^b$	Compd.	Solv. ^a	$\lambda(10^{-3} [\theta])^b$		
(1a)	C	237 (-1.07)	(1b)	C	272.5 (0.006), 253 (-0.84), 233 (-0.49)		
	HFP	235.5 (-0.51), 212.5sh (-0.39)		M	270 (0.005), 244 (-0.15), 226 (-0.28)		
(2a)	C	242 (-1.84), 224sh (-0.41)		H ₂ O	252.5 (0.14), 225 (-0.20)		
	HFP	238.5 (-1.05), 213 (-0.47)		HFP	243 (0.44), 220 (-0.40)		
(3a)	C	242 (0.47), 218 (2.07)		(2b)	C	272. (0.04), 259 (-0.86), 227.5 (-0.60)	
	HFP	253.5 (0.036), 233.5 (-1.09), 212 (2.47)	M		249 (0.53), 226 (-0.38)		
(4a)	C	233 (-8.65)	H ₂ O		250 (1.09), 224 (-0.17)		
			HFP		245 (1.59), 221 (-0.83)		
(5a)	C	245 (2.72), 212 (-1.10)	(3b)		CD	256 (-3.21), 228.5 (2.89)	
	CD	243 (2.13), 214 (-1.51)		M	253.5 (-4.23), 226 (2.678)		
	A	242 (2.11), 211 (-1.84)		H ₂ O	251 (-5.76), 221 (3.85)		
	HFP	238 (2.60), 209 (-1.43)		HFP	248.5 (-6.54), 220 (3.54)		
(7a)	CD	241.5 (-0.69), 220 (0.59)		(4b) ^c	CD	251 (-5.86), 225sh (5.22)	
	(8a)	C	243sh (1.46), 228.5 (2.24)		M	250 (-5.97)	
		(8b)	CD	255.5 (-1.48), 233 (1.18)	(5b)	CD	270 (-0.41), 262.5 (0.03), 232 (-4.61)
			M	248.5 (-1.54), 227.5 (1.08)		M	250sh (-3.37), 230 (-6.43)
		H ₂ O	268 (0.03), 250 (-0.39), 230 (0.99)	HFP	244 (-3.93), 226.5 (-4.43)		
HFP	262 (0.30), 244 (-0.06), 231.5 (0.42)	(5c)	CD	251sh (-4.05), 230 (-6.04)			
(11)	D		254 (2.17), 234.5 (-1.12)	(6)	D	258 (0.95), 226 (-1.73)	
	M	260 (1.02), 237 (-2.44), 221 sh(-0.30)	M		254.5 (0.85), 218.5 (-1.34)		
	H ₂ O	270 (0.05), 235 (-3.33)	H ₂ O	252 (1.58), 216 (-1.44)			
	HFP	270 (0.21), 234 (-0.79)	HFP	255 (0.71), 218 (-1.72)			
(7b)	CD	265 (-2.62), 234 (1.88)	(9)	M	255 (0.66), 229 (-2.54)		
	M	260 (-2.46), 232.5 (1.72)		H ₂ O	248.5 (1.59), 214 (-2.34)		
	H ₂ O	260 (-0.84), 231 (1.14)		(12)	CD	270.5 (1.12), 241.5 (-2.92)	
	HFP	253 (-1.42), 229 (0.71)			M	271.5 (0.38), 242.5 (-3.38), 223sh (-0.70)	
(8b)	CD	255.5 (-1.48), 233 (1.18)			H ₂ O	275 (0.09), 244 (-4.77)	
	M	248.5 (-1.54), 227.5 (1.08)	HFP		273.5 (0.12), 243 (-4.75)		

^a A, acetonitrile; C, cyclohexane; CD, cyclohexane-dioxane (4:1); D, dioxane; HFP, hexafluoropropan-2-ol. ^b The highest intensity vibronic bands.

^c Partially racemic sample; the data are not corrected for optical purity.

A_2 , is a combination of $n_+-\pi^*$, $n_--\pi^*$ and higher energy excited states. Although the first is allowed, the calculated oscillatory strength is very low in agreement with the low intensity of these bands. The strong absorption at 190 nm exhibited by imides corresponds to the $\pi-\pi^*$ transition whereas anhydrides do not show $\pi-\pi^*$ absorption in the accessible u.v. region. The weak solvent effect confirms these assignments. α -Substitution of succinimides causes shifting of the $n-\pi^*$ and $\pi-\pi^*$ bands to lower energies as a result of the twisting of the chromophore. However, mutual differences are small and are not diagnostic for stereochemical predictions.

C.D. Spectra.—The results of c.d. measurements are given in Table 2. Contrary to the expectation, the shape of the c.d. curves of structurally related anhydrides and imides differ significantly in many cases, especially in the region of the lowest energy $n-\pi^*$ transition. However, the C.e. signs of the higher energy c.d. bands are the same for all related compounds of both classes. The c.d. curves are strongly dependent on the solvent polarity and the nature of the substituents (Figures 2—6) pointing to the flexibility of the rings. The different conformational behaviour of anhydrides and imides is probably a primary reason for the differences in the c.d. spectra of both systems. Generally, two bands with the opposite C.e. signs are observed in accordance with the opposite symmetry of the excited states involved in the two $n-\pi^*$ transitions. Nevertheless, some spectra consist of two bands with the same signs. Sjöberg and Obenius³ have

proposed the separation of such curves into the Gaussian components with opposite signs. However, a fine structure makes this separation difficult and, moreover, the resultant composite Gaussians differ significantly in half-width. Inspection of imide u.v. spectra reveals nearly the same half-width of the two $n-\pi^*$ bands (*ca.* 15 nm) and a similar width is expected for anhydrides. More likely an equilibrium between two conformers with different C.e. signs is responsible for such behaviour. A proper sector rule would be helpful in assigning the C.e. signs for each conformation. Although the helicity rule postulated by Sneath and co-workers² correctly predicts the C.e. signs of the twisted anhydride chromophore, the 12-sector rule proposed by them for the planar chromophore predicts opposite signs to those observed.^{3,8} The MM2 and diffraction data show only slight distortion of the chromophores from planarity which contrasts with the sizable twisting of the rings; therefore, it seems reasonable to assume that the main contribution to the C.e. arises from the ring chirality. In view of this a sector rule uniformly treating planar and twisted chromophores would be desirable.

According to Schellman's minimal symmetry requirements²⁸ a quadrant rule should operate for planar (C_{2v}) chromophores but the dynamic coupling model indicates that an octant rule is better.²⁹ On these grounds and with the experimental results for relatively rigid bicyclic compounds,⁸ the octant (antioctant) rule with the signs opposite to those known for ketones may be proposed for the lowest energy $n-\pi^*$ transition of planar

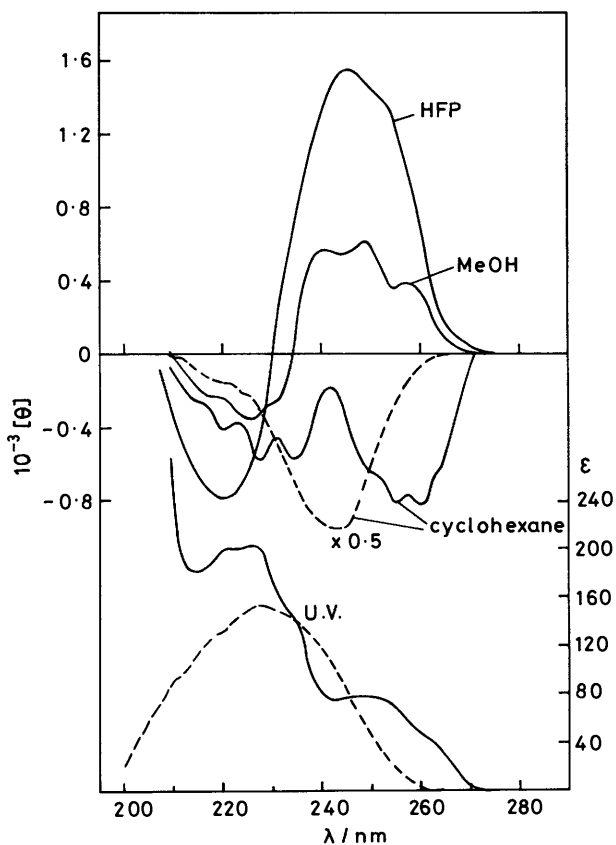


Figure 2. C.d. (upper curves) and u.v. spectra of the anhydride (2a) (broken lines) and the imide (2b) (solid lines)

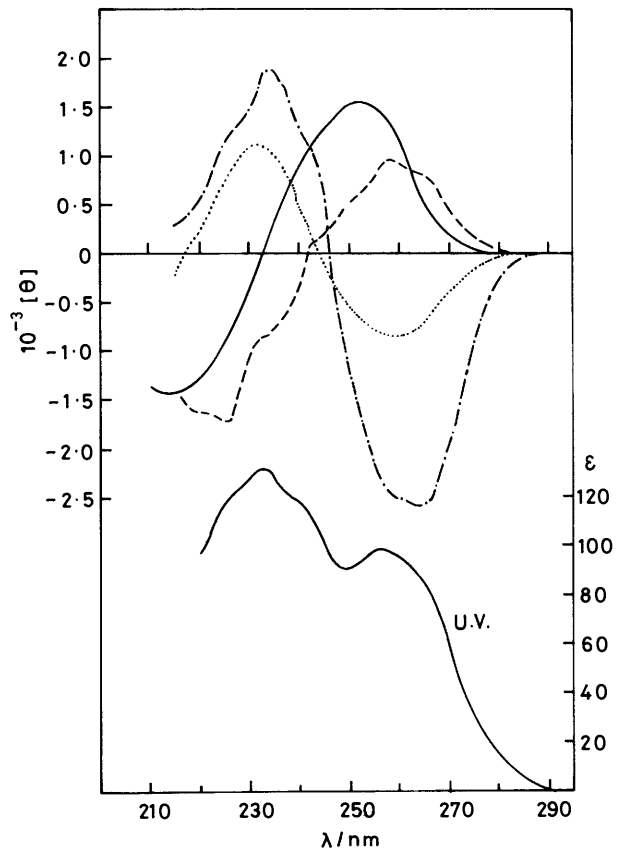


Figure 4. C.d. spectra of malimide (6) in water (—), and dioxane (---), c.d. of the imide (7b) in cyclohexane-dioxane (4:1) (---), water (···), and u.v. (lower curve) of (7b) in cyclohexane

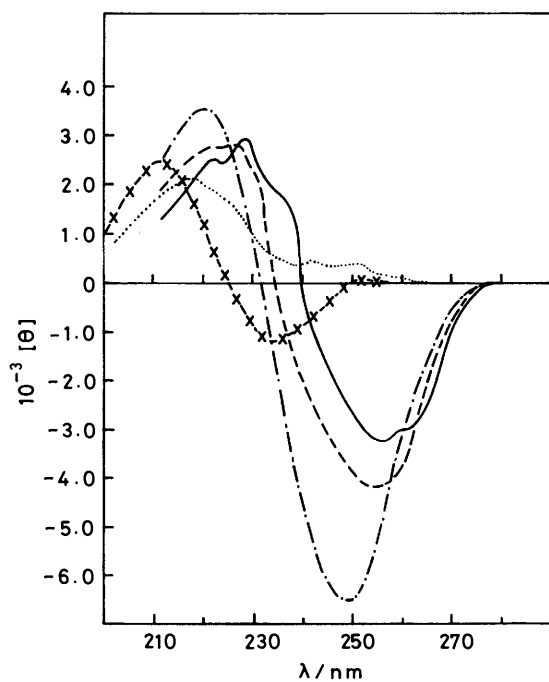


Figure 3. C.d. spectra of the anhydride (3a) in cyclohexane (···) and HFP (—x—x—), the imide (3b) in cyclohexane (—), methanol (---), and HFP (---)

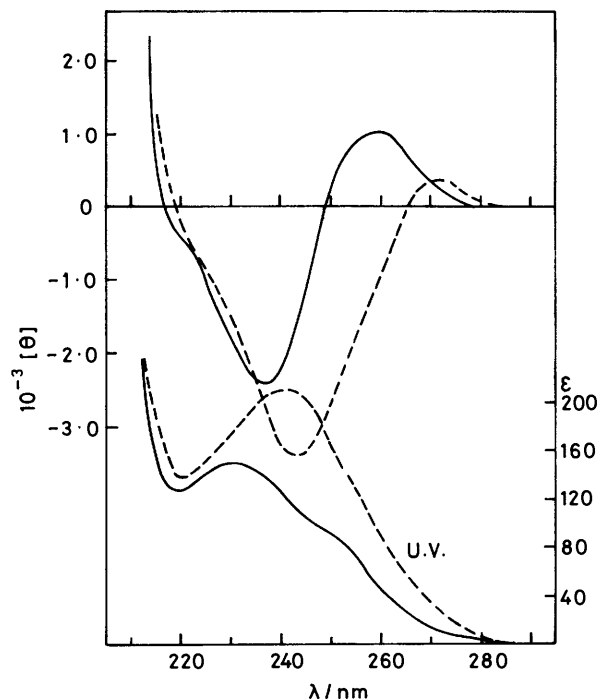


Figure 5. C.d. (upper curves) and u.v. spectra of imides (11) (solid lines) and (12) (broken lines) in methanol

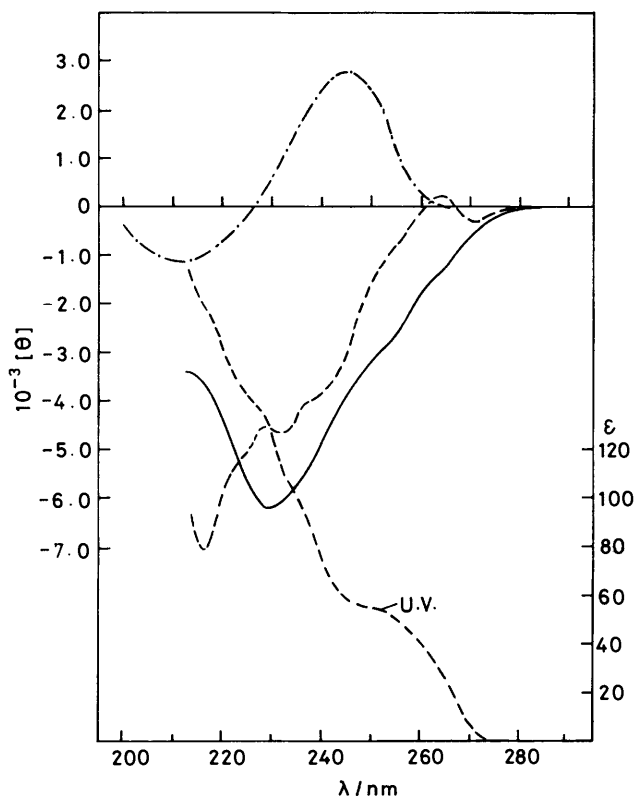


Figure 6. C.d. spectra of the anhydride (**5a**) in cyclohexane (— · — · —), imide (**5b**) in methanol (—), cyclohexane-dioxane (4:1) (— · — · —), and u.v. (lower curve) of (**5b**) in cyclohexane-dioxane (9:1)

anhydride and imide chromophores (Figure 7). The same rule but with the reversed signs should be suitable for the next $n-\pi^*$ transition. The contributions to C.e. of anhydrides and imides originate from three main sources: dissymmetrically placed substituents, a skewed ring, and inherent chirality of the chromophore. Fortunately, the inherent chirality of the chromophores does not require separate treatment since the sign of their contribution predicted by the Sznatzke chirality rule² is the same as the sign of the skewed ring contribution predicted by the octant rule and it can be treated as exerting the latest effect. Thus, the octant rule may be applied not only to planar but also to skewed chromophores.

Inspection of the octant projections of the two possible skewed conformers shows that the substituent and chiral ring contributions are of the same sign for the axial conformer and are opposite for the equatorial one. According to the Sznatzke hypothesis of spheres³⁰ the ring (chiral second sphere) acts more strongly than the substituents (chiral third sphere) and determines the C.e. sign as illustrated by c.d. of the bicyclic anhydride (**5a**). The strong ring contribution originates from the delocalization of MOs over the whole skeleton. The spectra of the anhydrides (**1a**) and (**2a**) point to the predominance of the equatorial conformer in the equilibrium although polar solvents enhance the amount of the axial form. An axial conformation of the anhydrides is favoured by bulky substituents as shown by c.d. of the *t*-butyl substituted succinic anhydride (**3a**) especially in polar media (Figure 3). The reported³ opposite C.e. signs shown by (*R*)-ethyl- and (*S*)-isopropylsuccinic anhydrides at low temperatures can be explained analogously, the first adopts the equatorial and the second the axial conformation. The flexibility of the succinimide ring is reflected in the strong solvent dependence of the spectra of (**1b**) and (**2b**) (Figure 2). A negative C.e. sign at 250 nm observed in cyclohexane solution gradually becomes positive when going to polar solvents, along with a shift in the conformational equilibrium from the equatorial to the axial form. In the case of the imide (**3b**) the axial conformer predominates in all types of solvents (Figure 3). The strong magnitude of C.e. shown by (**3b**) in polar media may result from enhanced twisting of the ring induced by solvation.

Intriguing behaviour is shown by malimide (**6**) and its *O*-methyl derivative (**7b**); these closely related species show almost mirror image c.d. curves (Figure 4). α -*t*-Butoxysuccinimide (**8b**) behaves similarly to compound (**7b**). A negative c.d. at 250 nm points to a predominance of the equatorial conformer for (**6**) which may be stabilized by intramolecular hydrogen bonding between the neighbouring hydroxy and carbonyl groups. Analogously, hydrogen bonding between protonated amino and carbonyl groups is expected for aspartimide (**9**) which shows the same C.e. signs as (**6**). The etherification of the hydroxy function favours the axial conformation for the anhydride (**7a**), and the imides (**7b**) and (**8b**), as shown by positive c.d. in the long-wavelength region and this result remains in accordance with the MM2 prediction. The local dipole-dipole interaction between the imide group and substituents bearing heteroatoms causes solvent dependence of the spectra. An increased dielectric constant of the solvent diminishes these interactions giving an enhanced population of the equatorial form in polar media; compare the spectra of (**8b**) in water and hexafluoropropan-2-ol (HFP). Even stronger

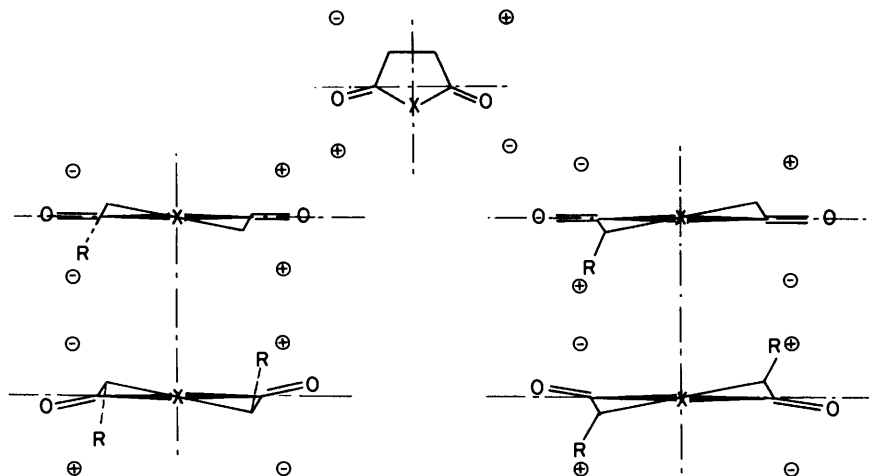


Figure 7. The octant projections of skewed conformers as substituted succinic anhydrides and imides

dipole-dipole interactions, stabilizing the diequatorial form, are expected for tartramide (11) and its *O,O'*-di-*t*-butyl derivative (12). This was evidenced by the C.e. signs and unusual u.v. spectra of these compounds, the higher energy $n-\pi^*$ band is shifted to the red and strongly overlaps with the second $n-\pi^*$ band which is slightly shifted to the blue. Both bands are still discernible in the imide (11) but only a single band at 240 nm of double intensity is observed for compound (12) (Figure 5). The change of the $n-\pi^*$ transition energy in (11) and (12) probably results from the electronic interactions of electron lone pairs on substituent oxygens with the chromophore orbitals in these high symmetry molecules. The strongest overlap between corresponding orbitals occurs in the diequatorial form since the substituent oxygens are in close proximity to the imide group. The corresponding c.d. curves exhibit a rather complicated shape (Figure 5) pointing to a conformational equilibrium; strong negative c.d. near 240 nm corresponds to the two overlapping $n-\pi^*$ transitions in the diequatorial conformer whereas positive c.d. near 270 nm results for diaxial conformer contribution.

The spectra of the bicyclic imide (5b) reveals some unexpected features, in that its strong c.d. and C.e. signs are negative in both $n-\pi^*$ regions (Figure 6) whereas the octant rule predicts a sequence of positive and negative C.e.s. The weak positive C.e. at 260 nm which is observed only in cyclohexane disappears upon *N*-methylation [*cf.* (5c)].† The conformational equilibrium is improbable for such rigid compounds although, small solvent-induced deformations of the chromophore geometry may occur.

The imide chromophore in (5b) is more strongly twisted than in other imides,²⁰ and may, therefore, be a source of abnormal behaviour in the compound. The distortion of the chromophore from planarity causes perturbation of its electronic states, *e.g.* the higher energy states ($\pi-\pi^*$) mixes with $n-\pi^*$ states. Small energy differences between the $\pi-\pi^*$ and $n-\pi^*$ states facilitates such mixing which may be responsible for the sign reversal of the long-wavelength C.e. This is only a tentative explanation, however, needing confirmation from the c.d. of anhydride (5a). The behaviour of compound (5a), contrasts with that of imide (5b) and, despite its strong twisting, shows a typical bisignate c.d. curve where the signs agree with those predicted by the octant rule. The reason is the much larger energy gap between anhydride $\pi-\pi^*$ and $n-\pi^*$ transitions which makes mixing of the electronic states difficult.

Appendix

The molecular mechanics calculations for anhydrides require an extension of Allinger's MM2 parameterization.¹² The torsional parameters V_1 , V_2 , and V_3 for angle types 1-3-6-3 and 7-3-6-3 (atom types assigned according to the ref. 12b), and minimum energy bond angles for angle types 1-3-6, 1-3-7, 6-3-7, and 3-6-3 are required. Recently, Ivanov and Pojarlieff¹³ have developed such a parameterization for succinic anhydrides. However, attempts to apply these parameters to acyclic and six-membered ring compounds failed, *e.g.*, almost planar anhydride moieties resulted for acetic and camphoric anhydrides whereas diffraction methods showed considerable distortion of the chromophore from planarity in these compounds.^{31,32} Also, calculated bond angles for six-membered rings differ from experimental values. The inadequacy of the reported parameters follows from the method of optimization which was used for rigid bicyclic five-membered ring anhydrides.¹³ For this reason new torsional parameters were obtained following the

procedure of Pearlstein and Hopfinger,³³ the potential energy of acetic anhydride was calculated as a function of the O=C-O-C torsion angle by the MNDO¹⁴ method followed by estimation of the minimum energy bond angles to obtain agreement with experimental values for acetic, succinic, 1-oxa-cyclohexane-4-spirocyclopentane-2,6-dione (close analogue of glutaric anhydride), and camphoric anhydrides. The following values were obtained: $V_1(1-3-6-3) - 47.9$ kJ mol⁻¹, $V_2(1-3-6-3) - 13.44$ kJ mol⁻¹, $V_3(1-3-6-3) - 7.12$ kJ mol⁻¹, $V_1(7-3-6-3) = V_2(7-3-6-3) = V_3(7-3-6-3) 0.0$ kJ mol⁻¹, $V_0(1-3-6) 113.0^\circ$, and $V_0(3-6-3) 114.0^\circ$. The bending force constant $k_0(3-6-3) 0.75$ m dyn Å rad⁻², the minimum energy bond angles $\theta_0(1-3-7) 129.4^\circ$ and $\theta_0(6-3-7) 117.5^\circ$, minimum energy bond lengths $l_0(3-6) 1.375$ Å and $l_0(3-7) 1.195$ Å were taken unchanged from the Ivanov and Pojarlieff paper.¹³ A satisfactory reproduction of the X-ray geometries of succinic,¹⁵ tetramethylsuccinic,²³ 1-oxa-cyclohexane-4-spirocyclopentane,³⁴ and camphoric³² anhydrides was achieved. The calculated dihedral angle between two acetyl planes in acetic anhydride is 68.9° compared with 78.8° obtained by electron diffraction.³¹

Experimental

C.d. spectra were recorded on a Jasco J-20 spectropolarimeter. U.v. measurements were performed on a Beckman 3600 spectrophotometer. N.m.r. spectra were taken on a Varian EM-360A (60 MHz) spectrometer with tetramethylsilane as internal standard. I.r. absorptions were taken with a Zeiss UR-10 spectrophotometer. Anhydrides (1a), (2a), (4a), (5a), and (7a) were obtained by the literature methods.^{3,35-37} The configurations of the parent succinic acids were already known.³⁸⁻⁴¹ The configuration of (-)-*t*-butylsuccinic acid was deduced from that known for its dimethyl ester.⁴² Succinimides were obtained from corresponding monoamides under very mild conditions (action of thionyl chloride in DMF at -70 to 5° C) adopting the procedure of Shealy *et al.*⁴³

(R)-2-Methylsuccinic Anhydride (1a).—M.p. $65-66^\circ$ C; $[\alpha]_D^{20} + 32.1^\circ$ (*c* 3 in CHCl₃) {lit.,³ m.p. $67.5-68.5^\circ$ C; $[\alpha]_D^{20} + 32.6^\circ$ (*c* 16.0 in dioxane); lit.,³⁵ $[\alpha]_D^{30} + 32.6^\circ$ (*c* 1.77 in CHCl₃)}.

(R)-2-Methylsuccinimide (1b).—Gaseous ammonia was passed over a solution of the anhydride (1a) (1.0 g) dissolved in benzene (10 ml) after which the mixture was evaporated. The residue was dissolved in DMF (20 ml) and the solution cooled to -70° C when thionyl chloride (1.0 ml) was added; the mixture was then left for 3 h at -5° C. After this the DMF was evaporated under reduced pressure and the residue was chromatographed on silica gel with benzene-ethyl acetate (4:1) as eluant. The title product (0.52 g) was crystallized from toluene, m.p. 78° C [lit.,²⁵ (racemate) m.p. 62° C]; $[\alpha]_D^{20} + 29.4^\circ$ (*c* 2 in CHCl₃); $\nu_{\max.}(\text{CCl}_4)$ 3 430, 3 230br, 1 745, and 1 735 cm⁻¹; $\delta_{\text{H}}(\text{CDCl}_3)$ 9.36 (1 H, br, NH), 3.2-2.0 (3 H, complex m), and 1.34 (3 H, d, Me) (Found: C, 53.0; H, 6.2; N, 12.6. C₅H₇NO₂ requires C, 53.1; H, 6.2; N, 12.4%).

(2R,3R)-2,3-Dimethylsuccinic Anhydride (2a).—M.p. 107° C (from toluene-hexane); $[\alpha]_D^{20} + 104^\circ$ (*c* 2 in dioxane) {lit.,³ m.p. $107-107.5^\circ$ C; $[\alpha]_D^{20} + 105.3^\circ$ (*c* 1.88 in dioxane)}.

(2R,3R)-2,3-Dimethylsuccinimide (2b).—The imide (2b) was obtained in a similar manner to compound (1b), and had m.p. 103° C (from toluene) [lit.,⁴⁴ (racemate) m.p. 111° C]; $[\alpha]_D^{20} + 53.6^\circ$ (*c* 1.4 in CHCl₃); $\lambda_{\max.}(\text{cyclohexane})$ 249.5 (ϵ 78) and 225.5 nm (200); $\lambda_{\max.}(\text{MeOH})$ 247.5 (ϵ 80) and 220 nm (235); $\nu_{\max.}(\text{CCl}_4)$, 3 430, 3 200br, 1 795, 1 750, and 1 730 cm⁻¹; $\delta_{\text{H}}(\text{CDCl}_3)$ 9.11 (1 H, br, NH), 2.43 (2 H, m), and 1.32 (6 H, d, 2 × Me) (Found: C, 56.35; H, 7.2; N, 10.9. C₆H₉NO₂ requires C, 56.7; H, 7.1; N, 11.0%).

† *N*-Methylation may increase twisting of the imide group due to steric interactions between *N*-methyl and neighbouring carbonyls.

(R)-2-*t*-Butylsuccinic Acid.—The resolution of racemic acid⁴⁵ with (–)-1-phenylethylamine (two crystallizations of monosalt from ethanol–diethyl ether) gave laevorotatory acid, m.p. 122–123 °C [lit.,⁴⁵ (racemate) m.p. 133 °C]; $[\alpha]_D^{20}$ –26.5° (*c* 5 in acetone); δ_H (CDCl₃) 10.9 (2 H, s, CO₂H), 2.66 (3 H, complex m), and 0.96 (9 H, s, CMe₃).

Dimethyl (R)-2-*t*-Butylsuccinate.—(R)-*t*-Butylsuccinic acid was esterified with diazomethane, b.p. 105 °C at 25 mmHg; $[\alpha]_D^{20}$ –12.3° (*c* 5 in EtOH) {lit.,⁴² (enantiomer) b.p. 120 °C (bath temperature) at 2 mmHg; $[\alpha]_D$ +12.4° (*c* 0.582 in EtOH)}.

(R)-2-*t*-Butylsuccinic Anhydride (3a).—(R)-2-*t*-Butylsuccinic acid (1.4 g) was refluxed with acetyl chloride (10 ml) for 0.5 h after which the mixture was evaporated to dryness and the residue crystallized from hexane to give the *title product* (1.15 g), m.p. 63–64 °C; $[\alpha]_D^{20}$ –11.4° (*c* 4 in C₆H₆); λ_{max} (cyclohexane) 225 nm (ϵ 130); ν_{max} (CCl₄) 1 875 and 1 800 cm^{–1}; δ_H (CCl₄) 2.8 (3 H, m) and 1.04 (9 H, s, CMe₃) (Found: C, 61.6; H, 7.6. C₈H₁₂O₃ requires C, 61.5; H, 7.7%).

(R)-2-*t*-Butylsuccinimide (3b).—Gaseous ammonia was passed over a solution of the anhydride (3a) (0.70 g) dissolved in benzene (5 ml) after which the mixture was evaporated. The residue was acidified with hydrogen chloride dissolved in diethyl ether and the resultant monoamide esterified with diazomethane. The product was dissolved in methanol (10 ml) containing sodium methoxide (obtained from 0.06 g sodium) and after 10 min at room temperature the solvent was evaporated off. The residue was acidified with dilute hydrochloric acid and extracted with diethyl ether. The extracts were dried (Na₂SO₄), evaporated to dryness, and crystallized from toluene–hexane to give the imide (3b) (0.41 g), m.p. 124–125 °C; $[\alpha]_D^{20}$ +28.5° (*c* 2 in CHCl₃); λ_{max} (cyclohexane) 249 (ϵ 105) and 223 nm (140); λ_{max} (H₂O) 194.5 nm (15 000); ν_{max} (CCl₄) 3 430, 3 220br, 1 790, 1 735, and 1 720 cm^{–1}; δ_H (CDCl₃) 9.1 (1 H, br, NH), 2.62 (3 H, m), and 1.0 (9 H, s, CMe₃) (Found: C, 61.8; H, 8.65; N, 8.95. C₈H₁₃NO₂ requires C, 61.9; H, 8.4; N, 9.0%).

(R)-2-Phenylsuccinic Anhydride (4a).—M.p. 82 °C (from toluene–hexane); $[\alpha]_D^{20}$ –98.7° (*c* 2 in C₆H₆) {lit.,³⁵ m.p. 82 °C (enantiomer) $[\alpha]_D^{20}$ +99.8° (*c* 0.75 in C₆H₆)}

(R)-2-Phenylsuccinimide (4b).—The imide (4b) was obtained in a similar manner to compound (1b). After cyclization the reaction mixture was poured onto 10% aqueous sodium acetate. The precipitate was filtered off, washed with water, and crystallized from toluene–hexane to give the *title product*, m.p. 83–94 °C (partially racemic) [lit.,⁴⁶ (racemate) 90 °C]; $[\alpha]_D^{20}$ 151° (*c* 2 in EtOH); ν_{max} (CCl₄) 3 430, 3 240br, 1 795, 1 745, and 1 735 cm^{–1}; δ_H (CDCl₃) 9.23 (1 H, br, NH), 7.26 (5 H, s, Ph), 4.03 (1 H, m, *J*_{AX} 9.2 and *J*_{BX} 5.8 Hz, C_αH), and 3.5–2.5 (2 H, m, *J*_{AB} 18.0 Hz, CH₂) (Found: C, 68.6; H, 5.4; N, 8.0. C₁₀H₃NO₂ requires C, 68.6; H, 5.2; N, 8.0%).

(S)-trans-Cyclohexane-1,2-dicarboximide (5b).—The imide (5b) M.p. 163 °C from toluene–hexane; $[\alpha]_D^{20}$ –127° (*c* 2 in C₆H₆) {lit.,³⁶ m.p. 164 °C; $[\alpha]_D^{20}$ –76.6° (in acetone)}; λ_{max} (cyclohexane–dioxane (9:1)) 224 nm (ϵ 67); ν_{max} (CCl₄) 1 875 and 1 805 cm^{–1}.

(S)-trans-Cyclohexane-1,2-dicarboximide (5b).—The imide (5b) was obtained in a similar manner to compound (4b) and had m.p. 204 °C (from ethyl acetate); $[\alpha]_D^{20}$ –127.5° (*c* 1 in MeOH); λ_{max} (cyclohexane–dioxane (9:1)) 249sh (ϵ 55) and 228.5 nm (129); λ_{max} (MeOH) 247sh (ϵ 71) and 255sh (215); λ_{max} (H₂O)

198 nm (ϵ 15 300); ν_{max} (CCl₄) 3 430, 3 240br, 1 790, and 1 750 cm^{–1}; δ_H ([²H₆]acetone) 9.30 (1 H, br, NH), 2.39 (2 H, m, 2 × CHCO), and 2.2–1.0 (8 H, complex m) (Found: C, 62.85; H, 7.4; N, 9.1. C₈H₁₁NO₂ requires C, 62.7; H, 7.2; N, 9.1).

(S)-trans-N-Methylcyclohexane-1,2-dicarboximide (5c).—The anhydride (5a) was converted into the corresponding *N*-methylamide by the reaction of ethanolic methylamine and was refluxed with an excess of acetyl chloride for 0.5 h to give the *title product*, m.p. 131 °C (from toluene–hexane); $[\alpha]_D^{20}$ –161° (*c* 1.5 in CHCl₃); ν_{max} (CCl₄) 1 790 and 1 715 cm^{–1}; δ_H (CCl₄) 2.84 (3 H, s, NMe), 2.22 (2 H, m, 2 × C_αH), and 2.0–1.0 (8 H, complex m) (Found: C, 64.8; H, 7.8; N, 8.3. C₉H₁₃NO₂ requires C, 64.65; H, 7.8; N, 8.4%).

(S)-2-Methoxysuccinic Anhydride (7a).—B.p. 125 °C at 15 mmHg; $[\alpha]_D^{20}$ –104° (*c* 2 in C₆H₆) {lit.,³⁷ b.p. 130–132 °C at 17 mmHg; $[\alpha]_D^{20}$ –103.3° (*c* 5 in C₆H₆)}; ν_{max} (CCl₄) 1 875 and 1 800 cm^{–1}; δ_H (CDCl₃) 4.47 (1 H, m, C_αH), 3.57 (3 H, s, CO₂Me), and 3.5–2.6 (2 H, complex m, CH₂).

(S)-2-Methoxysuccinimide (7b).—The imide (7b) was obtained in a similar manner to compound (1b) and had m.p. 70 °C (from toluene–hexane); $[\alpha]_D^{20}$ –76° (*c* 0.8 in MeOH); λ_{max} (cyclohexane) 257 (ϵ 99) and 233 nm (123); λ_{max} (MeOH) 252 (ϵ 82) and 225 nm (139); ν_{max} (CCl₄) 3 420, 3 230br, 1 795, and 1 740 cm^{–1}; δ_H ([²H₆]acetone) 10.0 (1 H, br, NH), 4.50 (1 H, m, *J*_{AX} 8.2 and *J*_{BX} 5.4 Hz, C_αH), 3.65 (3 H, s, OMe), and 2.3–3.4 (2 H, complex m, *J*_{AB} 18.5 Hz, CH₂) (Found: C, 46.3; H, 5.7; N, 10.9. C₅H₇NO₃ requires C, 46.5; H, 5.5; N, 10.85%).

(S)-2-*t*-Butoxysuccinic Anhydride (8a).—Following the procedure of Beyerman and Bontekoe⁴⁷ (–)-dimethyl malate (Fluka) (8.1 g, 50 mmol) was dissolved in methylene dichloride (20 ml), and the solution cooled to 0 °C; concentrated sulphuric acid (0.5 ml) and liquid isobutene (40 ml) were then added. The bottle was stoppered and left for 4 days at room temperature. After cooling, the reaction mixture was washed with saturated aqueous NaHCO₃, dried (MgSO₄), and evaporated. The residue was distilled under reduced pressure to give *dimethyl (S)-2-*t*-butoxysuccinate* (10.2 g), b.p. 120–122 °C at 15 mmHg; $[\alpha]_D^{20}$ –56.8° (neat); δ_H (CCl₄) 4.33 (1 H, t, C_αH), 3.65 (6 H, s, 2CO₂Me), 2.52 (2 H, m, CH₂CO), and 1.10 (9 H, s, CMe₃). The above ester (6.54 g, 30 mmol) was hydrolysed with potassium hydroxide (4.5 g, 80 mmol) in methanol (30 ml) and water (10 ml) for 1 h at room temperature. The methanol was then evaporated off and the residue cooled to 0 °C and acidified with dilute hydrochloric acid; it was then extracted with diethyl ether. The extracts were dried (MgSO₄) and evaporated to give (S)-2-*t*-butoxysuccinic acid (4.95 g) as an oil, δ_H (CDCl₃) 10.7 (1 H, m, s, CO₂H), 4.39 (1 H, t, C_αH), 2.77 (2 H, m, CH₂), and 1.15 (9 H, s, CMe₃). The above acid was dissolved in acetic anhydride and set aside for 24 h at room temperature. It was then evaporated and the residue crystallized from toluene–hexane to give the *title product* (3.6 g), m.p. 64 °C; $[\alpha]_D^{20}$ –51.5° (*c* 2 in C₆H₆); ν_{max} (CCl₄) 1 865 and 1 800 cm^{–1}; δ_H (CCl₄) 4.67 (1 H, m, *J*_{AX} 6.8 and *J*_{BX} 8.4 Hz, C_αH), 3.4–2.3 (2 H, complex m, *J*_{AB} 18.4 Hz, CH₂), and 1.20 (9 H, s, CMe₃) (Found: C, 55.6; H, 7.0. C₈H₁₂O₄ requires C, 55.8; H, 7.0%).

(S)-2-*t*-Butoxysuccinimide (8b).—The imide (8b) was obtained in a similar manner to compound (4b) and had m.p. 108–109 °C; $[\alpha]_D^{20}$ –62° (*c* 2 in CHCl₃); λ_{max} (cyclohexane) 251sh (ϵ 82) and 231 nm (126); λ_{max} (MeOH) 248sh (ϵ 75) and 226 nm (145); λ_{max} (H₂O) 194.5 nm (ϵ 18 300); ν_{max} (CCl₄) 3 425, 3 235br, 1 800, and 1 735 cm^{–1}; δ_H (CDCl₃) 9.13 (1 H, br, NH), 4.43 (1 H, m, *J*_{AX} 8.0 and *J*_{BX} 5.6 Hz, C-H), 3.2–2.2 (2 H, complex m, *J*_{AB} 18.4 Hz, CH₂), and 1.19 (9 H, s, CMe₃) (Found:

C, 55.8; H, 7.9; N, 8.55. $C_8H_{13}NO_3$ requires C, 56.1; H, 7.65; N, 8.2%.

(S)-2-Hydroxysuccinimide (9).—The imide (8) (1.4 g) was dissolved in trifluoroacetic acid (TFA) (5 ml) and set aside for 3 h at room temperature. It was then evaporated and the residue crystallized from ethyl acetate–hexane to give the *title product* (0.8 g), m.p. 95 °C; $[\alpha]_D^{20} -92^\circ$ (c 2 in MeOH) {lit.,⁴ m.p. 96–97 °C; $[\alpha]_D^{20}$ (c 1 in MeOH)}; λ_{max} . [cyclohexane–dioxane (9:1)] (250 (ϵ 90) and 228 nm (132); λ_{max} . (MeOH) 248.5 (ϵ 69) and 224 nm (126); λ_{max} . (H₂O) 194.5 nm (ϵ 16 300); ν_{max} . (CHCl₃) 1 735 cm⁻¹; δ_H ([²H₆]acetone) 9.84 (1 H, br, NH), 4.97 (1 H, br, OH), 4.63 (1 H, m, J_{AX} 8.4 and J_{BX} 5.2 Hz, C₂H), and 3.2–2.2 (2 H, complex m, J_{AB} 18.4 Hz, CH₂).

(S)-2-(Benzyloxycarbonylamino)succinimide (10).—(S)-N-Benzyloxycarbonylasparagine (Fluka) was converted into the imide (10) analogously to compound (4b) and had m.p. 79–81 °C (from toluene); $[\alpha]_D^{20} -41.5^\circ$ (c 2 in EtOH) {lit.,^{48a} m.p. 79–81 °C; lit.,^{48b} m.p. 80–81 °C; $[\alpha]_D^{20} -43^\circ$ (c 3.6 in EtOH)}.

(S)-2-Aminosuccinimide Hydrobromide (9).—The cleavage of the N-benzyloxycarbonyl group in compound (10) with hydrogen bromide in acetic acid gives the *title product*, m.p. 218 °C; λ_{max} . (MeOH) 245 (ϵ 75) and 230sh nm (163); δ_H ([²H₆]DMSO) 12.0 (1 H, br, NH), 9.03 (3 H, br, +NH₃), 4.7 (1 H, m, C₂H), and 3.12 (2 H, m, CH₂); free base, m.p. 141–143 °C (decomp.); $[\alpha]_D^{20} -76^\circ$ (c 0.6 in MeOH) {lit.,^{48a,b} m.p. 143 °C (decomp.); $[\alpha]_D^{20} -77^\circ$ (in MeOH)}.

Dimethyl (2R,3R)-2,3-Di-t-butoxysuccinate.—This ester was obtained from (+)-dimethyl tartrate (Aldrich) in a similar manner to that described for dimethyl (S)-2-t-butoxysuccinate and had m.p. 62–64 °C (from ethyl acetate–hexane); $[\alpha]_D^{25} +34.3^\circ$ (c 3 in MeOH); δ_H (CCl₄) 4.02 (2 H, s, 2 × C₂H), 3.61 (6 H, s, 2 × CO₂Me), and 1.10 (18 H, s, 2 × CMe₃) (Found: C, 57.5; H, 9.25. C₁₄H₂₆O₆ requires C, 57.9; H, 9.0%).

(2R,3R)-2,3-Di-t-butoxysuccinimide (12).—The above ester was hydrolysed to the corresponding dicarboxylic acid, transformed into the anhydride with the procedures analogous to that described for anhydride (8a), and, without purification, was immediately converted into imide (12) analogously to compound (4b). The *title product* had m.p. 154 °C (from toluene–hexane); $[\alpha]_D^{20} +205^\circ$ (c 1 in CHCl₃); λ_{max} . (cyclohexane) 242 nm (ϵ 180); λ_{max} . (MeOH) 240.5 (ϵ 205); λ_{max} . (H₂O) 194 nm (ϵ 15 500); ν_{max} . (CCl₄) 3 415, 3 235br, 1 805, 1 755, and 1 740 cm⁻¹; δ_H (CDCl₃) 8.50 (1 H, br, NH), 4.30 (2 H, s, 2 × C₂H), and 1.23 (18 H, s, 2-CMe₃) (Found: C, 58.9; H, 8.7; N, 5.8. C₁₂H₂₁NO₄ requires C, 59.2; H, 8.7; N, 5.8%).

(2R,3R)-2,3-Dihydroxysuccinimide (11).—The imide (11) was obtained from compound (12) by TFA cleavage of t-butoxy groups with a procedure analogous to that described for compound (9). The *title product* had m.p. 200 °C (with decomp.); $[\alpha]_D^{20} 202^\circ$ (c 0.5 in H₂O) {lit.,⁴ m.p. 205–206 °C; $[\alpha]_D 200.9^\circ$ (c 2 in H₂O)}; λ_{max} . (MeOH) 249sh (ϵ 98) and 231.5 nm (150); ν_{max} . (KBr) 3 460br, 3 390br, 3 245br, 1 810, and 1 735 cm⁻¹.

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