Optical Activity in βγ-Unsaturated Ketones. Part 2.[1] Effect of the Magnitude and Energy of the Electric Transition Dipole Moment in the Aromatic Groups in 1- and 1,5-Substituted 9,10-Ethano-9,10-dihydroanthracen-11-one Derivatives

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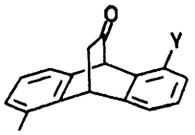
In 1- or 1,5-substituted 9,10-ethano-9,10-dihydroanthracen-11-one derivatives, the alteration of the substituents on the benzene ring brings about a change of the magnitude of the transition dipole moment and the transition energy in the aromatic chromophore without much alteration of the direction of the transition dipole moment. We synthesized optically active derivatives of the title compounds, determined their absolute configuration, studied the effects on the optical activity, and analysed them by application of dynamic and static coupling mechanisms. The optical activity was found to depend mainly on the magnitude of the transition dipole moment.

In Part 1,[1] we clarified the effect of the direction of the transition dipole moment of a perturber on the optical rotatory power, but the effect of the magnitude of the transition dipole moment remained unclear. In the 9,10-ethano-9,10-dihydroanthracen-11-one (EDA-11-one) derivative (1), an alteration in the nature of the substituents X and Y brings about changes in the transition dipole moment of the aromatic chromophore without much change in the direction of polarization, since the skeleton is fairly rigid and of defined geometry. In this paper, we describe the preparation of a series of EDA-11-one derivatives and the determination of the absolute configuration and analysis of the optical rotatory power by the use of the method described in Part 1,[1] which has been developed by Höhn and Weigang,[2] Schellman,[3] and Buckingham and Stiles.[4]



(1)

Synthesis and Absolute Configuration of 1- *and* 1,5-*Substituted* 9,10-*Ethano*-9,10-*dihydroanthracen*-11-*ones*.—The anthracene derivative (2a)[5] or (2b)[6,7] and α-acetoxyacrylonitrile[8] were heated at 160° to give Diels–Alder adducts. In the case of (2a), two types of crystals, m.p. 210—211° [(3a) or (4a)] and 158—160° [(4a) or (3a)] were isolated in the ratio 1 : 1, but other isomers [(5a) and/or (6a)] could not be isolated in pure form. Mild alkaline hydrolysis[9] of each of the crystalline adducts (3a) and (4a)

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[1] Part 1, S. Hagishita and K. Kuriyama, *J.C.S. Perkin II*, 1977, 1937.

[2] E. G. Höhn and O. E. Weigang, jun., *J. Chem. Phys.*, 1968, **48**, 1127.

[3] J. A. Schellman, *Accounts Chem. Res.*, 1968, **1**, 144.

[4] A. D. Buckingham and P. J. Stiles, *Accounts Chem. Res.*, 1974, **7**, 258.

[5] S. Akiyama, S. Misumi, and M. Nakagawa, *Bull. Chem. Soc. Japan*, 1962, **35**, 1826; E. A. Coulson, *J. Chem. Soc.*, 1930, 1931.

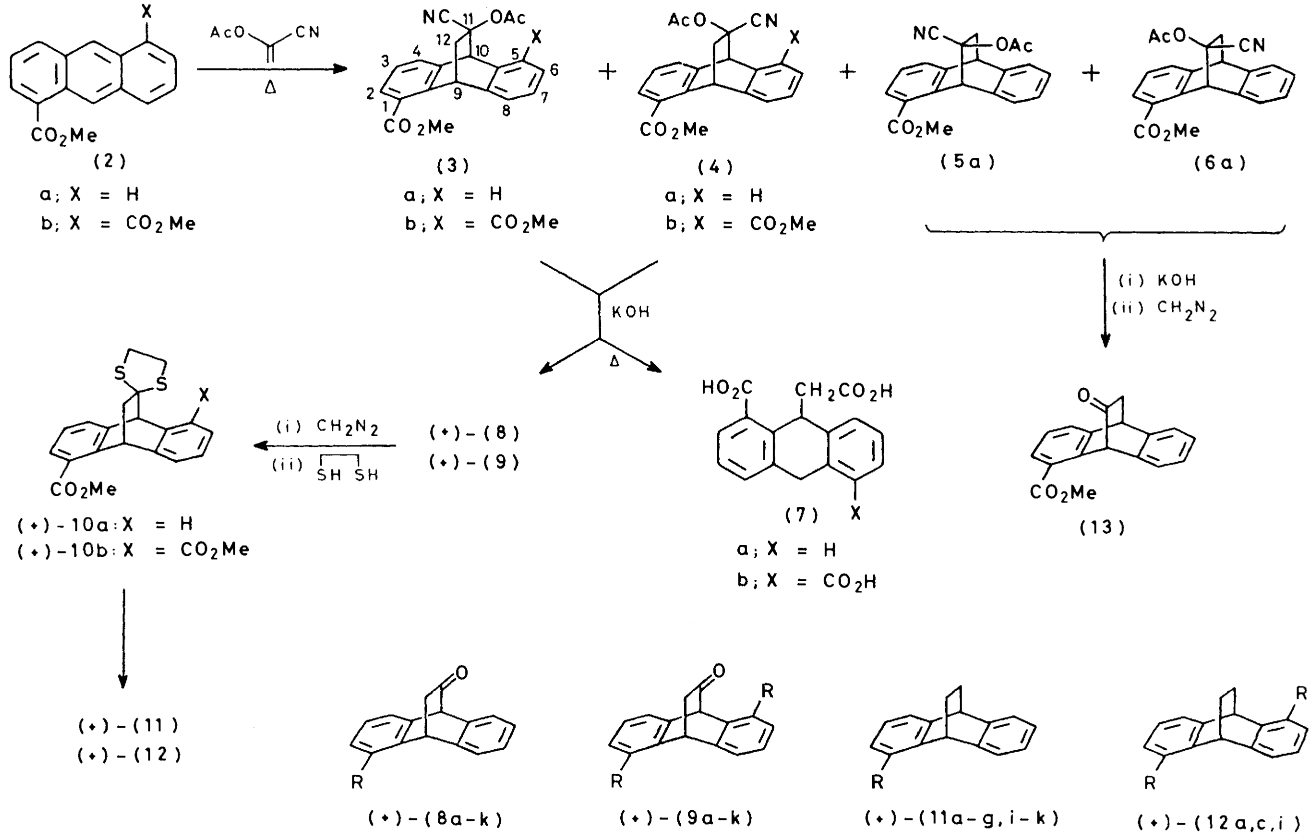
[6] Y. Shimizu, H. Tatemitsu, F. Ogura, and M. Nakagawa, *J.C.S. Chem. Comm.*, 1973, 22.

[7] S. Hagishita and K. Kuriyama, *Tetrahedron*, 1972, **28**, 1435.

[8] R. M. Nowak, *J. Org. Chem.*, 1963, **28**, 1182.

[9] M. A. Qaseen, N. A. Rogers, and A. A. Othman, *Tetrahedron*, 1968, **24**, 4535; P. F. Hudrlik, A. M. Hudrlik, and C.-N. Wan, *J. Org. Chem.*, 1975, **40**, 1116.

yielded the same keto-carboxylic acid (8a). But when the total reaction mixture was treated in the same way followed by esterification, the two kinds of the carboxylic esters (8a) and (13) were obtained in the ratio 5.3 : 1. This shows that the two isolated crystals are epimeric at C-11 and that the Diels–Alder reaction also gives the adducts (5a) and/or (6a). The epimeric relation of the two crystalline adducts (3a) and (4a) was also supported by their n.m.r. spectra, in which the bridgehead proton at C-9 showed the signal (t, *J* 3 Hz) to lower field than that of C-10 (s). However it was impossible to assign the configuration at C-11 by means of n.m.r. spectra owing to the almost identical pattern in both cases.



a; R = CO_2H
b; R = COCl
c; R = $CONH_2$
d; R = CN
e; R = CON_3
f; R = NCO
g; R = $NHCO_2Bu^t$
h; R = NH_2
i; R = CO_2Me
j; R = CH_2OH
k; R = CO_2Metal

In the case of (2b), two sets of crystals A, m.p. 227° and B, m.p. 175—177°, were isolated in pure form in the ratio *ca.* 1 : 1 by analysis of the n.m.r. spectrum. A comparison of the proton resonances of the acetoxy-group, τ 8.08 and 8.12, and that of the bridgehead proton, vicinal to the acetoxy-group, τ 2.68 and 2.80, for isomers A and B, respectively, suggests that the former has the *endo*-acetoxy-*exo*-nitrile configuration (4b) and the latter the *exo*-acetoxy-*endo*-nitrile configuration (3b).

When the hydrolysis of adducts (3) and (4) was carried out under more drastic conditions than the procedure of Rogers,[9] the product obtained was the 9,10-dihydroanthracene derivative (7). Similar results have already been reported by Cristol [10] and Vaughan.[11]

The optical resolution of the keto-carboxylic acid (8a) was tried with various kinds of optically active amines * and pseudo-ephedrine turned out to be the most effective. The (+)-enantiomer, $[\alpha]_D$ +121.3°, was obtained in pure form. In the case of the keto-dicarboxylic acid (9a), ephedrine is found to be best after many trials and gave the (+)-enantiomer, $[\alpha]_D$ +233°. (+)-EDA-1-carboxylic acid (+)-(11a) and (+)-EDA-1,5-dicarboxylic acid (+)-(12a), which are without a carbonyl group, were prepared from (+)-8a and (+)-9a through the esters (+)-(8i) and (+)-(9i) and then the dithioacetals (+)-(10a) and (+)-(10b), respectively. The (+)-keto-carboxylic acids (+)-(8a) and (+)-(9a) can be assigned the 9*R*,10*S*-configuration since compounds (+)-(11a) and (+)-(12a) have already been shown to have the 9*R*,10*S*- and 9*R*,10*R*-configurations,[7,12,13] respectively.

The substituted, optically active derivatives were

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* Cinchonidine, dehydroabietylamine, (+)-phenethylamine, brucine, ephedrine, pseudoephedrine, and quinine.

[10] S. J. Cristol and R. K. Bly, *J. Amer. Chem. Soc.*, 1960, **82**, 6155.

[11] W. R. Vaughan and M. Yoshimine, *J. Org. Chem.*, 1957, **22**, 528.

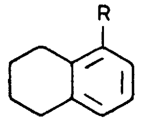
[12] J. Paul and K. Schlögl, *Monatsh.*, 1973, **104**, 274.

[13] H. Tatemitsu, F. Ogura, and M. Nakagawa, *Bull. Chem. Soc. Japan*, 1973, **46**, 915.

prepared by transformation of the carboxy-group as shown in the Scheme.

Compounds (14a—g) were also prepared to measure their u.v. spectra.

U.v. and C.d. Spectra.—Table 1 gives the u.v. and c.d. spectra of the compounds prepared. The u.v. spectrum of compound (+)-(8j) shows absorption maxima at *ca.* 300 and *ca.* 270 nm with fine structure and these two are well separated. Since (+)-(11j), which is without a keto-function, has only an absorption corresponding to the shorter wavelength, the longer wavelength peak cannot be attributed to one of the transitions produced by dipole–dipole coupling of the two aromatic chromophores but to the n–π^* transition



(14)

a; R = CO_2H
b; R = CO_2Me
c; R = COCl
d; R = $CONH_2$
e; R = CN
f; R = CH_2OH
g; R = NH_2

TABLE 1

U.v. and c.d. spectra

Compound	Solvent	U.v. λ/nm (ε)	C.d. λ/nm (Δε)
(+)-(8a)	MeOH	318sh (355), 306sh (829), 287 (2 140), 275 (1 750), 268sh (1 380), 232sh (10 100), 207 (36 900)	319sh (−0.409), 303 (−1.33), 282 (+6.07), 228 (+19.6), 215 (−32.3), 204 (+10.3)
(+)-(8b)	Iso-octane	321sh (1 280), 310 (2 730), 301 (2 950), 278sh (2 330), 255sh (9 880), 247 (11 100), 210sh (26 000)	322 (−3.47), 315 (−2.48), 305sh (+2.88), 294 (+8.01), 288 (+8.35), 278 (+8.70), 244 (+9.62), 237 (+15.0), 219 (−57.5)
(+)-(8c)	MeOH	318sh (346), 306 (701), 296sh (843), 275 (1 580), 268sh (1 340), 205 (45 000)	321sh (−0.32), 306sh (−0.79), 298 (−1.01), 277 (+4.40), 269sh (+1.99), 226 (+15.1), 212 (−35.9)
(+)-(8d)	CH_3CN	317 (451), 306 (803), 290 (2 660), 283 (2 540), 274sh (1 830), 267sh (1 290), 235sh (10 900), 206 (44 700)	316 (−0.481), 304 (−1.55), 297 (−2.06), 281 (+7.99), 228 (+26.1), 215 (−68.5)
(+)-(8h)	MeOH	317sh (339), 306 (677), 295sh (846), 248sh (9 690), 213sh (28 800), 200 (36 800)	319 (−0.285), 308 (−0.342), 275 (+2.50), 247 (+9.54), 228 (+21.7), 213 (−13.7)
(+)-(8i)	Iso-octane	321 (494), 309 (961), 298sh (2 180), 288 (2 600), 275sh (1 880), 268sh (1 490), 225sh (17 700), 207 (40 500)	321 (−0.819), 308 (−2.14), 300 (−1.98), 285 (+6.62), 278sh (+5.46), 270sh (+3.33), 262sh (+2.47), 232 (+26.7), 217 (−53.4)
(+)-(8j)	MeOH	317sh (333), 306 (629), 297 (667), 273 (955), 268 (977), 261sh (773), 255sh (576), 204 (46 500)	318sh (−0.177), 307 (−0.287), 298 (−0.273), 276 (+1.50), 273 (−0.22), 270 (+0.32), 265 (−0.44), 259 (−0.27), 252 (−0.11), 221 (+11.0)
(+)-(8k)	MeOH		295 (−0.808), 278 (+2.86), 276 (+0.993), 225 (+14.8)
(+)-(9a)	MeOH	322sh (439), 310sh (1 060), 287.5 (3 370), 228sh (18 700), 208.5 (42 500)	329 (−0.080), 320sh (+0.234), 294 (+4.02), 282 (+1.78), 270 (+1.41), 237 (+6.73), 212 (+48.0)
(+)-(9b)	Dioxan	314 (4 450), 305 (4 600), 251 (19 300), 214 (28 600)	324 (+4.52), 311 (+8.08), 307sh (+7.32), 291 (+1.97), 272 (+2.09), 261 (−2.45), 245 (+15.3), 233 (+13.2), 216 (+19.6)
(+)-(9c)	Dioxan	321 (457), 309 (789), 297sh (1 020), 281 (2 380), 209.5 (42 600)	321 (−0.618), 309 (−0.789), 284 (+2.40), 242 (+5.88), 223sh (+13.1)
(+)-(9d)	Dioxan	322 (577), 308 (1 110), 291 (3 900), 281 (3 640), 226sh (27 000), 210 (94 800)	323 (−0.289), 317sh (−0.248), 308sh (+0.25), 290 (+4.89), 280 (+2.59), 250 (−0.15), 237 (+8.00), 222 (+20.2), 212 (+43.9)
(+)-(9h)	MeOH–KOH	297 (4 330), 231sh (19 000), 214 (36 500)	304 (+7.12), 263 (−5.01), 237 (+13.3), 216 (+24.9)
(+)-(9i)	Dioxan	322 (694), 309sh (1 480), 299sh (3 110), 289 (4 170), 227sh (23 100), 210 (46 200)	331 (−0.09), 320sh (+0.448), 308sh (+1.45), 295 (+3.79), 283sh (+1.87), 272sh (+1.31), 236 (+5.85), 225sh (+11.2), 213 (+57.5)
(+)-(9j)	MeOH	316sh (377), 307 (658), 297.5 (703), 277 (992), 271 (1 010), 205 (44 800)	319 (−0.080), 296sh (+0.062), 286sh (+0.153), 275 (+0.955), 269 (+1.13), 239 (+1.40), 232 (−1.98), 228 (−1.70), 208 (+28.9)
(+)-(9k)	MeOH–KOH	304sh (786), 282 (1 720), 235sh (1 180)	316sh (−0.412), 309 (−0.430), 290 (+0.454), 275sh (+12.9), 230sh (+17.5), 216 (+54.3)
(+)-(11a)	MeOH	286 (2 580), 230sh (11 500), 203 (41 500)	286 (+2.59), 238sh (+8.82), 220 (+18.4)
(+)-(11c)	MeOH	275 (1 810), 268sh (1 320), 255 (1 150), 230sh (7 450), 201 (42 400)	281 (+1.44), 234 (+6.75), 210! (+14.4)
(+)-(11d)	CH_3CN	288.5 (3 310), 281 (3 190), 235sh (11 200), 225 (14 200), 204.5 (52 400)	289 (+3.63), 282sh (+3.54), 238 (+6.81), 220 (+11.0)
(+)-(11j)	MeOH	274.5 (1 390), 271.5 (1 290), 267 (1 200), 230sh (3 830), 208sh (33 600)	275 (−1.23), 267 (−0.55), 262 (+0.347), 231 (+7.23), 215! (+13.6)
(+)-(11k)	MeOH–KOH	273sh (1 660), 265 (1 330)	284 (+0.581), 232sh (+9.28), 214 (+31.9)
(+)-(12a)	MeOH	280 (2 330), 230sh (14 300)	291 (+8.28), 230sh (+19.6), 222 (+7.49), 209 (+25.0)
(+)-(12c)	Dioxan	283 (3 170), 225sh (21 900), 208 (37 600)	284 (+5.32), 225 (+29.9)
(+)-(12i)	MeOH	291 (5 160), 229 (21 100), 206sh (40 700)	292 (+9.68), 232 (+20.5), 224 (+21.4), 210 (+27.3)

! Indicates lowest wavelength limit of measurement (not necessarily a maximum or minimum in the c.d. curve).

of the carbonyl group. The shorter wavelength absorption is therefore the benzene ^1L_b transition. This assignment is supported by the red shift of the absorption maximum of the shorter wavelength in compounds with stronger perturbing substituents as shown in (+)-(8a—i).

The sign of the Cotton effect in the n–π^* transition is always negative for (+)-(9R,10S)-(8a—k). But the octant diagram for the ketone shows that the substituent itself is in the positive region, although it is close to the nodal surface (Figure 1). The sign seems to be determined by a difference in the electronic properties of the aromatic rings rather than the substituent itself.

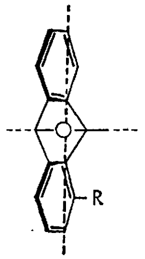


FIGURE 1

The c.d. band in the region 260—300 nm, which is related to the ^1L_b transition, is positive for this configuration except for the fine structure of compound (+)-(8j). It is interesting that the rotational strength is always larger than that of the corresponding compounds (11), which are without a carbonyl group. The difference in the rotational strength is larger in compounds with stronger perturbers. Compound (+)-(11j), with a weak perturbing group, exhibits a negative Cotton effect at 275 nm with fine structure and the corresponding carbonyl derivative (+)-(8j) shows a positive sign, although the magnitude is small. This means that the interaction between the carbonyl and the aromatic groups makes a positive contribution to the Cotton effect in this configuration.

We observed two further absorption maxima at *ca.* 230 and 210 nm in both series of compounds (+)-(8) and (+)-(11). The former absorption is always a shoulder of the latter. The Cotton effects in compounds (+)-(11) are positive for both absorptions but in the carbonyl compounds (+)-(8) the Cotton effects are positive for the shorter and negative for the longer wavelength. This negative Cotton effect in the shorter wavelength region is characteristic of the 9R,10S-1-substituted EDA-11-ones.

In the 1,5-disubstituted EDA-11-one derivatives, the c.d. spectra are more complex. For the n–π^* transition, derivatives (+)-(9a), (+)-(9d), (+)-(9i), and (+)-(9j) show positive and negative Cotton effects for the shorter and longer wavelengths, respectively; for compounds (+)-(9c) and (+)-(9k) both signs are negative and for compound (+)-(9b) both are positive. In compound (+)-(9h), the Cotton effect completely overlaps that of the benzene transition and cannot be resolved. Thus, we cannot find a general relationship between the sign of the Cotton effect and the absolute configuration.

In the ^1L_b transition, all the compounds show a positive Cotton effect. The corresponding compound without a carbonyl group also exhibits a positive sign and the difference in magnitude seems to have no relation with the properties of the substituents. We cannot systematize the effects caused by the interaction between the carbonyl group and the two substituted benzene chromophores in this region.

Calculations.—We calculated the rotational strength by the method used in Part 1. The geometry of the skeleton is idealized as follows: aromatic C–C bond, 1.392 Å; C(1a)–C(9), C(4a)–C(10), C(5a)–C(10), C(8a)–C(9), C(10)–C(11), and C(11)–C(12) single bonds, 1.505 Å; C(9)–C(12) single bond, 1.533 Å, and C=O double bond, 1.22 Å; the planes C(9)–(C1a)–C(4a)–C(10), C(9)-(C8a)–C(5a)–C(10), and C(9)–C(12)–C(11)–C(10) are at 120° to each other; the origin of the co-ordinate system was taken as the centre of the C=O bond.

Table 2 gives the magnitude, the position, and the direction of the permanent dipole moment[14] used in the calculations. Since Nagakura and Baba[15] have pointed out that the permanent dipole moment of aniline is polarized 35° upward from the benzene ring, we calculated the static term with this value about two conformers for (8h) and four conformers for (9h). We took into consideration the n–π^*, n–σ^*, and π–π^* transitions as the local carbonyl transitions and used values of the electric and magnetic transition dipole moments and quadrupole moment described in Part 1.[1]

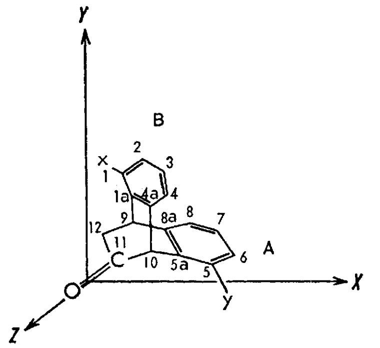


FIGURE 2

Since the transition dipole moments of the local aromatic chromophores play an important role in the rotational strength, it is necessary to evaluate them more precisely. We assumed the transition energies and dipole strengths of the tetralin derivatives (14b, e, f, and g) as the values of each aromatic chromophore and used these values, as shown in Table 2.

Tanaka has shown that the 230 nm band of benzoic acid is polarized 6.5° outward from the long axis towards

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[14] A. L. McClellan, 'Table of Experimental Dipole Moments,' Freeman, San Francisco, 1963.

[15] S. Nagakura and H. Baba, *J. Chem. Soc. Japan*, 1950, **71**, 527.

TABLE 2

Magnitude, position, and direction of the permanent dipole moment and energy and magnitude of the transition dipole moment of the local chromophores

R	10^8 Magnitude [14] (c.g.s.)	Position [a] (Å)	Direction [b] (°)		Transition dipole moment λ/nm [$10^{20} \times \mu$ (c.g.s.)]			
			ring A	ring B				
H					267 (6.54)	213 (24.5)	199 (38.2)	193 (39.0)
CN	4.00	1.455	0	180	283 (11.5)	233 (28.0)	198 (41.7)	205 (42.6)
CO_2Me	1.83	1.48	−110	−70	285 (11.9)	236 (26.4)	207 (35.5)	196 (38.1)
CH_2OH	1.31	2.235 ± 1.238 [d]	162.4	17.6	268 (7.27)	216 (26.7)	202 (38.6)	194 (38.8)
NH_2	1.52	1.41	−145 [c]	−35	286 (10.5)	239 (33.7)	208 (49.6)	199 (44.8)
			145	35				

[a] Distance from the bonding aromatic carbon atom. [b] The angle with the line C(1)—C(4) in the benzene plane. [c] In the plane perpendicular to the benzene ring containing C(1) and C(4). [d] Distance perpendicular to the C–C single bond in the benzene plane.

TABLE 3

Experimental and calculated c.d. spectra, main configurations, and magnitude of the contribution of the local transitions in 1-substituted EDA-11-ones

Compound	Obs.		Calc.		Main configuration	Contributions							
	λ/nm	$10^{40}R$ (c.g.s.)	λ/nm	$10^{40}R$ (c.g.s.)		n–π*	n–σ*	π–π*		^1L_b	^1L_a	^1B_b	^1B_a
(+)-(8d)	297	−1.98	298.8	−13.5	n–π*		0	−0.47	A	+0.43	+7.47	+3.46	+13.87
									B	−3.00	−13.47	−3.33	−18.53
	281	+9.30	285.1	+2.53	^1L_bA	+3.01	+0.58	+0.06					
			267.0	−0.50	^1L_bB	−0.40	−0.18	−0.02					
	228	+43.8	233.7	+14.1	^1L_aA	+15.68	+5.18	−0.66					
	215	−43.5	214.5	−28.2	^1L_aB	−8.87	−8.49	−0.57					
(+)-(8h)	308	−0.39	298.8	−23.9	n–π*		0	−0.86	A	+0.44	+7.63	+3.61	+14.19
									B	−2.57	−21.55	−5.89	−19.20
	275	+2.73	286.1	+2.14	^1L_bA	+2.57	+0.50	+0.05					
			267.1	−0.37	^1L_b	−0.43	−0.15	−0.02					
	228	+62.0	239.2	+22.6	^1L_aA	+23.88	+6.25	−0.98					
	213	−10.5	214.6	−135	^1L_aB + ^1B_bA								
			213.0	+136	^1B_bA + ^1L_aB								
(+)-(8i)	308	−1.40	297.7	−3.73	n–π*		0	+0.52	A	+0.41	+7.18	+3.26	+13.31
									B	−3.38	−10.79	−3.08	−11.48
	285	+8.60	285.1	+2.85	^1L_bA	+3.42	+0.52	+0.06					
			267.0	+0.01	^1L_bB	−0.34	−0.21	−0.02					
	232	+53.5	235.7	+19.8	^1L_aA	+11.5	+2.16	0					
	217	−33.4	213.6	−44.2	^1L_aB	−7.04	−7.00	−0.94					
(+)-(8j)	298	−0.49	297.6	−2.03	n–π*		0	−0.03	A	+0.42	+7.33	+3.29	+13.59
									B	−0.50	−9.07	−3.30	−13.58
	276	+0.95	268.2	+0.50	^1L_bA	+0.60	+0.17	+0.02					
	265	−0.26	267.0	−0.53	^1L_bB	−0.28	−0.21	−0.03					
	221	+10.9	218.4	−8.16	^1L_aA + ^1L_aB								
			212.6	−13.1	^1L_aB + ^1L_aA								

the carbonyl group.[16] The conformation of the methoxycarbonyl group in (+)-(8i) and (+)-(9i) seems to be fixed to some extent by steric interaction with the bridgehead proton in the *peri*-position. The preferred conformation of the methoxycarbonyl group is assumed such that the carbonyl group is directed towards the bridgehead. On this consideration, the long axis polarization is inclined at 6.5° towards the bridgehead. In other compounds, the transition of the long-axis polarization is directed along the line of C(1)–C(4) to the centre of the benzene ring and that of the short-axis one is perpendicular to the line in the benzene plane.

RESULTS AND DISCUSSION

Table **3** gives the observed and the calculated c.d. spectra and the main configuration for the transition in the monosubstituted carbonyl compounds (+)-(8d and h—j). The transition of lowest energy is attributable to the n–π* transition from the calculations and this coincides with the observed assignment. There is good agreement in sign between the observed and the calculated Cotton effects in this region, although the magnitude is larger for the calculated values. Further, the rotatory power is chiefly produced by $\vec{\mu}$—$\vec{m}$ coupling between the magnetic moment of the n–π* transition and the electric moment of the perturbing local transitions. The extent of the contribution to rotational strength can be seen by the results shown in Table **3**. Each of the transitions of the unsubstituted benzene chromophore in (+)-(8d and h—j) contributes toward a positive effect and naturally has an almost constant value regardless of the nature of the substituents on the other benzene ring. The long-axis polarization contributes more strongly than the short-axis one and the effect of the direction has already been discussed in Part 1.[1] The transitions of the substituted benzene ring always contribute a negative effect

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[16] J. Tanaka, *Bull. Chem. Soc. Japan*, 1963, **36**, 833.

and the size of the contribution is related to the magnitude of the electric transition dipole moment. Thus, the rotational strength seems to be mainly determined by the difference between the magnitude of the electric dipole moments of the corresponding transitions in rings A and B (Figure 2), but also to some extent by that between the corresponding transition energies.

TABLE 4

Experimental and calculated c.d. spectra, main configurations, and magnitude of the contribution of the local transitions in 1,5-disubstituted EDA-11-ones

Compound	Obs.		Calc.		Main configuration	Contribution [$10^{40}R$ (c.g.s.)]						
	λ/nm	$10^{40}R$ (c.g.s.)	λ/nm	$10^{40}R$ (c.g.s.)		n–σ^*	π–π^*		^1L_b	^1L_a	^1B_b	^1B_a
(+)-(9d)	323	+0.38	299.1	−1.70	n–π^*	0	−2.01	B	+3.13	+13.76	+19.00	+3.69
	308	−0.21						A	−3.06	−13.75	−18.98	−3.61
	290	+6.18	286.1	+0.26	^1L_bA + ^1L_bB							
	280	+3.50	284.1	−1.02	^1L_bA + ^1L_bB							
	237	+0.84	236.2	−8.75	^1L_aA + ^1L_aB							
	222	+3.30	230.9	−0.02	^1L_aA + ^1L_aB							
	212	+59.0	210.2	−41.4	^1L_bA + ^1L_bB							
(+)-(9i)	331	−0.09	298.3	+9.27	n–π^*	0	+4.35	B	+3.53	+13.71	+3.32	+14.63
	295	+6.88						A	−3.49	−10.72	−3.28	−11.45
	283	+1.63	286.2	+0.59	^1L_bA + ^1L_bB							
	272	+1.19	284.1	+0.67	^1L_bA + ^1L_bB							
	236	+3.80	236.9	−22.7	^1L_aA + ^1L_aB							
	225	+9.00	234.3	+24.3	^1L_aA + ^1L_aB							
	213	+65.9	212.2	+8.49	^1B_bA + ^1B_bB							
(+)-(9j)	319	+0.10	297.7	+1.45	n–π^*	0	+0.23	B	+0.54	+9.12	+3.53	+13.65
	286	−0.12						A	−0.50	−0.12	−3.31	−13.65
	275	−0.42	268.4	~0	^1L_bA + ^1L_bB							
	269	−1.88	267.7	−0.39	^1L_bA + ^1L_bB							
	239	−1.19	219.6	−17.1	^1L_aA + ^1L_aB							
	230	+1.65	214.4	−0.08	^1L_aA + ^1L_aB							
	208	−67.9	208.3	−7.98	^1B_bA + ^1B_bB							
(+)-(12i)	292	+18.9	286.3	~0	^1L_bA + ^1L_bB							
			283.9	~0	^1L_bA + ^1L_bB							
	232	+34.8	238.0	−27.9	^1L_aA + ^1L_aB							
	224	+26.1	233.5	+19.1	^1L_aA + ^1L_aB							
	210	+37.0	212.2	−0.04	^1B_bA + ^1B_bB							

TABLE 5

Experimental and calculated c.d. spectra and main configurations for the four kinds of conformers of 1,5-diamino-EDA-11-one

Compound	Experimental		Calculated					Configuration
	λ/nm	$10^{40}R$ (c.g.s.)	λ/nm	$10^{40}R$ (c.g.s.)	$10^{40}R$ (c.g.s.)	$10^{40}R$ (c.g.s.)	$10^{40}R$ (c.g.s.)	
(+)-(9h)	304	+16.2	300.3	+0.66	−0.02	−2.44	−3.12	n–π^*
			287.0	+0.33	+0.32	+0.27	+0.25	^1L_bA + ^1L_bB
	263	−11.6	285.3	−0.68	−0.68	−0.65	−0.58	^1L_bA + ^1L_bB
	237	+22.8	239.3	−16.8	−16.2	−19.2	−18.6	^1L_aA + ^1L_aB
			238.8	−0.35	−0.30	−0.68	−0.63	^1L_aA + ^1L_aB
	216	+49.3	219.3	+0.33	+0.29	+0.14	+0.12	^1B_bA + ^1B_bB
			208.1	−165	−160	−164	−160	^1B_bA + ^1B B

Since the point dipole of the transition is assumed to be at the centre of the benzene rings, the $\vec{\mu}$–$\vec{\mu}$ coupling mechanism through interaction between the two aromatic chromophores does not give rise to any optical rotatory power in the region of the benzene transitions except for (12i). Further, we have reported [7] that the charge transfer transition between two aromatic chromophores is possible in EDA derivatives by ' through space interaction ' and by ' through bond interaction ', and in addition to this direct contribution of the charge transfer transition to the optical activity, the sequence of the symmetric (A) and antisymmetric (B) combination, in the C_2 group, of the localized excitation energies of the two aromatic chromophores may be different from that obtained by exciton treatment, in which the electronic exchange is completely neglected. The Cotton effect is mainly produced from dipole–dipole couplings even in the presence of the electronic exchange in EDA derivatives but it happens occasionally that electron transfer between the chromphores brings about the reverse of the energy sequence of the A and B symmetries. This means that the coupling pattern turns into the opposite and leads to the opposite absolute configuration.

As we assumed that the point dipole moment is at the centre of the benzene rings and did not take into consideration electron exchange in the present work, it is impossible to explain the optical activity of compounds (12), which lack a carbonyl group, and also impossible to evaluate the Cotton effect in the region of the benzene transitions for compounds (8). But as the energies of the local chromophores are not degenerate in compounds (8) and (11), it can be deduced that the effect of the electronic transfer would be too small to reverse the transition energy sequence of the main configuration. We can estimate the optical rotatory power produced by the interaction between the local carbonyl transitions and the benzene transition. Experimentally, we can observe that the carbonyl compounds (8) have always a larger positive rotational strength than compounds (11) in the region of the ^1L_b transition. The calculated rotational strengths have the correct sign for all compounds (8) and are produced mainly by the $\vec{\mu}$–$\vec{m}$ coupling mechanism.

Tables 4 and 5 give the observed and calculated c.d. spectra and the main configuration of the transitions in the disubstituted carbonyl compounds (+)-(9d and h—j). In the 1,5-substituted EDA-11-ones, the corresponding local transitions of two aromatic chromophores are degenerate and have the same dipole strength. Therefore, the rotational strength is produced through the static term in this treatment.[2,4] But the rotational strength is very small compared with that calculated from consideration of the correct position of the point dipole, the electron exchange, and the magnetic transition moment produced perpendicular to the benzene ring in the short-axis transitions.[12,17,18] Therefore the calculated values are too unreliable to even guess the absolute configuration. However the nature of the transition is clear.

EXPERIMENTAL

I.r. spectra were taken with a JASCO model DS 402 G double-monochromatic spectrophotometer. Optical rotations were measured on a Perkin-Elmer polarimeter model 141 using a 1 dm cell. C.d. spectra were taken with a JASCO model ORD/UV-6 instrument. N.m.r. spectra were measured with a Varian A-60 spectrophotometer using tetramethylsilane as internal standard. U.v. spectra were measured with a Hitachi 323 spectrometer and far-u.v. spectra with a Beckman DK-2A spectrometer. Mass spectra were measured on a Hitachi RUM-6 single-focusing mass spectrometer. M.p.s are uncorrected.

Diels–Alder Reaction of the Anthracene Derivatives (2a *and* b).—A mixture of methyl anthracene-1-carboxylate[5] (47.6 g), freshly distilled α-acetoxyacrylonitrile (32.6 g), hydroquinone (1.0 g), and dry xylene (450 ml) was heated under reflux for 2 days under nitrogen. Insoluble materials were removed by filtration and the solvent was removed by distillation. The recovered anthracene derivative (16.0 g) was removed by filtration from a warm methanol solution. The crystalline adducts were collected by filtration from the cold solution and recrystallized twice from ethyl acetate to give a powder A, m.p. 210—211°. A small portion of the filtrate was chromatographed on thick silica gel plates [Merck GF; benzene–ethyl acetate (9 : 1)]. Crystals B, m.p. 158—160°, were obtained from the band with the largest R_F value. Oily materials were obtained from the band with next largest R_F value.

The ratio of isomers A and B was *ca.* 1 : 1 from the material isolated and when all the reaction mixture was treated with aqueous KOH at 40—50° and then esterified, the ratio of the keto-esters (8i) and (13) was 5.3 : 1 from the isolated yield.

Methyl 9,10-*dihydro*-9,10-*ethano*-12-*oxo*-*anthracene*-1-*carboxylate* (13) had m.p. 130—132°, $\nu_{max.}$ (Nujol) 1 725 and 1 715 cm^{-1}, τ(CDCl$_3$) 3.87(s), 5.41(t, *J* 3.0 Hz), 6.06(s), and 7.66(d, *J* 2.5 Hz) (Found: C, 77.7; H, 5.15. $C_{18}H_{14}O_3$ requires C, 77.7; H, 5.1%).

Crystals A had $\nu_{max.}$ (Nujol) 2 230, 1 748, 1 715, 1 258, 1 228, 1 216, and 1 028 cm^{-1}, τ(CDCl$_3$) 4.29(s), 4.90(s), 6.05, 7.30(dd, *J* 14.0 and 3.0 Hz), 7.90(dd, *J* 14.0 and 3.0 Hz), and 8.10(s) (Found: C, 72.5; H, 4.9; N, 3.95. Calc. for $C_{21}H_{17}NO_4$: C, 72.6; H, 4.95; N, 4.05%). Crystals B had $\nu_{max.}$ (Nujol) 2 230, 1 745, 1 724, 1 264, 1 225, and 1 033 cm^{-1} (Found: C, 72.45; H, 5.0; N, 3.9%).

Dimethyl anthracene-1,5-dicarboxylate[6,7] (21.5 g) was treated according to the same procedure and gave crystalline adducts (17.1 g), known from the n.m.r. spectrum to be a 1 : 1 mixture of the isomers (3b) and (4b). One isomer (4b), m.p. 227°, was fractionally recrystallized from ethyl acetate and the other (3b), m.p. 175—177°, from ethyl acetate–methanol. *Dimethyl* 1-*acetoxy*-1-*cyano*-9,10-*ethano*-9,10-*dihydroanthracene*-1,5-*dicarboxylate* had m.p. 227°, $\nu_{max.}$ (Nujol) 1 720, 1 709, 1 213, and 1 185 cm^{-1}, $\lambda_{max.}$ (dioxan) 291 (ε 4 210), 240sh (15 300), 227 (23 200), and 207 nm (39 200), τ([$^2H_6$]DMSO) 2.68(s), 3.33(t, *J* 3.0 Hz), 6.05(s), 6.10(s), 7.80(d, *J* 3.0 Hz), 8.08(s), and *ca.* 8.1 (Found: C, 68.25; H, 4.9; N, 3.4. $C_{23}H_{19}NO_6$ requires C, 68.15; H, 4.7; N, 3.45%). *Isomer* (3b) had m.p. 175—177°, $\nu_{max.}$ (Nujol) 1 578, 1 720, 1 709, 1 220, and 1 195 cm^{-1}, $\lambda_{max.}$ (dioxan) 290 (ε 4 160), 225 (22 700), and 208 nm (36 700), τ([$^2H_6$]DMSO) 2.80(s), 3.33 (t, *J* 2.5 Hz), 6.08(s), 7.73(d, *J* 3.0 Hz), *ca.* 8.1 and 8.12(s) (Found: C, 68.05; H, 4.7; N, 3.4%).

(±)-11-*Oxo*-*EDA*-1-*carboxylic Acid* (8a).—To 14% aqueous KOH (19 ml) was added a mixture of adducts (3a) and (4a), (4.8 g) in tetrahydrofuran (38 ml) and methanol (6.5 ml). The mixture was stirred at 40° for 5 h, cooled to room temperature, washed with chloroform, and acidified with concentrated HCl. The crystals were collected by filtration, washed with water, dried, and recrystallized from ethyl acetate to give a *powder* (2.74 g), m.p. 248°, $\nu_{max.}$ (Nujol) 1 727, 1 689, and 1 114 cm^{-1}, τ(CDCl$_3$) 3.98(t, *J* 3.0 Hz), 51.2(s), and 7.62(d, *J* 3.0 Hz) (Found: C, 77.35; H, 4.6. $C_{17}H_{12}O_3$ requires C, 77.25; H, 4.6%). The adduct of m.p. 158—160° gave the same carboxylic acid.

The oily adducts gave the *acid* of ester (13) as a powder, m.p. 246—248°, $\nu_{max.}$ (Nujol) 1 730, 1 685, and 1 095 cm^{-1} (Found: C, 77.0; H, 4.65%).

(±)-11-*Oxo*-*EDA*-1,5-*dicarboxylic Acid* (9a).—A mixture of adducts (3b) and (4b) (5.3 g) was treated according to the same procedure. Recrystallization from methanol gave a *powder* (3.0 g), m.p. >300°, *m/e* 308 (M^+), $\nu_{max.}$ (Nujol) 1 738 and 1 685 cm^{-1} (Found: C, 68.4; H, 4.1. $C_{18}H_{12}O_5$,0.5 H_2O requires C, 68.15; H, 4.15%).

When the adducts were heated under reflux in the same reagent, (1,5-*dicarboxy*-9,10-*dihydroanthracen*-9-*yl*)*acetic acid* (7b) was obtained as a powder, m.p. 246—248° (decomp), $\nu_{max.}$ (Nujol) 1 690 and 765 cm^{-1}, $\lambda_{max.}$ 281 (ε 1 700), 271.5 (1 730), 265 (1 430), 233sh (6 770), and 200 nm (48 100) (Found: C, 71.4; H, 5.0. $C_{17}H_{14}O_4$ requires C, 72.3; H, 5.0%).

Optical Resolution of the Carboxylic Acid (8a).—(−)-Pseudoephedrine (4.03 g) was added to a suspension of the carboxylic acid (8a) (6.6 g) in ethyl acetate (30 ml). The mixture was briefly warmed to give a clear solution and allowed to stand at room temperature overnight. The

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[17] D. J. Caldwell and H. Eyring, *Ann. Rev. Phys. Chem.*, 1964, **15**, 281.

[18] A. Moscowitz, A. Rosenberg, and A. E. Hansen, *J. Amer. Chem. Soc.*, 1965, **87**, 1813.

crystals were collected by filtration, washed with ethyl acetate, and dried. Recrystallization from methanol three times gave the pure diastereomer, $[\alpha]_D^{26}$ +65.9 ± 2.4° (MeOH; *c* 0.443).

The salt (4.32 g) was shaken with a mixture of dilute HCl and ethyl acetate. After the usual treatment, the oily residue was crystallized from benzene to give a powder, (2.56 g), m.p. 188—188.5°, $[\alpha]_D^{25}$ +121.3 ± 2.3° (MeOH; *c* 0.700), $\nu_{max.}$ (Nujol) 1 690 cm^{-1}.

Optical Resolution of the Carboxylic Acid (9a).—A mixture of the carboxylic acid (9a) (846 mg), ephedrine (967 mg), and ethanol (5 ml) was briefly heated. Ethyl acetate was added dropwise, until the solution became slightly cloudy. The mixture was allowed to stand for 2 days. The crystals were collected by filtration, washed with ethanol–ethyl acetate, and dried. Recrystallization three times from ethanol gave the diastereomer, $[\alpha]_D^{22}$ +80.7 ± 4.4° (MeOH; *c* 0.274).

The salt (81.4 mg) was shaken with dilute HCl at 60° for 10 min. The crystals were collected by filtration, washed with water, dried, and recrystallized from methanol to give a powder (29.4 mg), m.p. 310°, $[\alpha]_D^{20}$ +233.0 ± 12.9 (MeOH; *c* 0.212).

(+)-*Methyl* 11-*Oxo-EDA*-1-*carboxylate* [(+)-(8i)].—The (+)-carboxylic acid (8a) (0.5 g) was esterified with excess of diazomethane in the usual manner but the optically active ester (0.51 g) could not be crystallized, although the racemate did crystallize, m.p. 184—187°, $\tau(CDCl_3)$ 4.09(t, *J* 3.0 Hz), 5.16(s), 6.03(s), and 7.66(d, *J* 3.0 Hz) (Found: C, 77.5; H, 5.0. $C_{18}H_{14}O_3$ requires C, 77.7; H, 5.05%).

(+)-*Dimethyl* 11-*Oxo-EDA*-1,5-*dicarboxylate* [(+)-(9i)].—This had m.p. 166—167° (racemate m.p. 173—173.5°), $[\alpha]_D^{23.5}$ +220.7 ± 9.7° (MeOH; *c* 0.270), $\nu_{max.}$ (Nujol) 1 723 cm^{-1}, $\tau(CDCl_3)$ 3.80(s), 4.02(t, *J* 3.0 Hz), 6.03(s), and 7.65(d, *J* 3.0 Hz) (Found: C, 71.45; H, 4.8. $C_{20}H_{16}O_5$ requires C, 71.4; H, 4.8%).

(+)-1-*Methoxycarbonyl*-11-*oxo-EDA Ethylene Dithioacetal* [(+)-(10a)].—Boron trifluoride–ether (3 ml) was added to a solution of the (+)-ester [(+)-(8a)] (0.51 g), ethanedithiol (3 ml), and glacial acetic acid (5 ml) at room temperature. The mixture was left for 6 h, poured into water, and extracted with ether. The solution was washed with aqueous sodium carbonate and water and dried (Na_2SO_4). The oily residue was chromatographed on a thin silica gel plate (Merck GF$_{254}$; benzene) but could not be crystallized.

(+)-1,5-*Bismethoxycarbonyl*-11-*oxo-EDA Ethylene Dithioacetal* [(+)-(10b)].—The oily residue was obtained by the same procedure as for (+)-(10a) and was crystallized from methanol, m.p. 153—154°, $[\alpha]_D^{22}$ +166.2 ± 5.2° (dioxan; *c* 0.394), $\nu_{max.}$ (Nujol) 1 713 cm^{-1} (Found: C, 64.15; H, 5.0; S, 15.85. $C_{22}H_{20}O_4S_2$ requires C, 64.05; H, 4.9; S, 15.55%).

(+)-*EDA*-1-*carboxylic Acid* [(+)-(11a)].—A mixture of Raney nickel (W2; *ca.* 2.5 g), the dithioacetal [(+)-(10a)] (551 mg) and dioxan (5 ml) was heated under reflux for 17 h with stirring. The insoluble materials were removed by filtration and washed with ether. The solvent was removed by distillation from the filtrate. The oily ester could not be crystallized and was heated with 5% KOH in methanol (20 ml) under reflux for 2.5 h. Water (30 ml) was added and the mixture was acidified with dilute HCl and extracted with ether. The solution was washed with water, dried (Na_2SO_4), and concentrated by distillation. The crystalline residue was recrystallized from methanol–water to give a powder, m.p. 200—201°, $[\alpha]_D^{23}$ +191.2 ± 6.1° (EtOH; *c* 0.377) (lit.,[12] $[\alpha]_D$ +185.0° for the 9*R* configuration), $\nu_{max.}$ (Nujol) 1 690 cm^{-1} (Found: C, 81.5; H, 5.55. Calc. for $C_{17}H_{14}O_2$: C, 81.6; H, 5.55%).

(+)-*Dimethyl EDA*-1,5-*dicarboxylate* [(+)-(12b)].—The (+)-ethylene dithioacetal [(+)-(10b)] (80 mg) was desulphurized by the same manner as for (+)-(11a) and recrystallization from methanol gave crystals (14 mg), m.p. 117—119°, $[\alpha]_D^{25}$ +330 ± 23° (MeOH; *c* 0.160) identical with an authentic sample.[7]

(+)-11-*Oxo-EDA*-1-*carbonyl Chloride* [(+)-(8b)].—A mixture of the (+)-carboxylic acid [(+)-(8a)] (433 mg) and thionyl chloride (2 ml) was heated under reflux for 1.5 h. Excess of thionyl chloride was removed by distillation under reduced pressure. The crystalline residue was recrystallized from benzene–light petroleum, m.p. 130—133° (Found: C, 72.1; H, 3.9; Cl, 12.65. $C_{17}H_{11}ClO_2$ requires C, 72.2; H, 3.9; Cl, 12.55%).

(+)-11-*Oxo-EDA*-1,5-*dicarbonyl Chloride* [(+)-(9b)].—The dicarboxylic acid [(+)-(9a)] was treated according to the same procedure cited above. Recrystallization from benzene–heptane gave *crystals*, m.p. 177—179°, $\nu_{max.}$ (Nujol) 1 760 and 1 740 cm^{-1} (Found: C, 64.0; H, 2.95; Cl, 20.25. $C_{18}H_{12}Cl_2O_3$ requires C, 62.25; H, 3.5; Cl, 20.4%).

(+)-11-*Oxo-EDA*-1-*carboxamide* [(+)-(8c)].—A solution of the (+)-acid chloride [(+)-(8b)] (430 mg) in dry tetrahydrofuran (5 ml) was added to concentrated NH_4OH (10 ml) at 0° with stirring. The mixture was stirred at 0° for 20 min. The crystals were collected by filtration, washed with water, dried, and recrystallized from ethyl acetate to give a *powder* (305 mg), m.p. 264—265° (decomp), $[\alpha]_D$ +103.3 ± 3.4° (dioxan; *c* 0.419), $\nu_{max.}$ (Nujol) 3 405, 3 180, 1 715, 1 680, 1 655, and 1 629 cm^{-1} (Found: C, 77.0; H, 4.95; N, 5.35. $C_{17}H_{13}NO_2$ requires C, 77.55; H, 5.0; N, 5.3%).

(+)-11-*Oxo-EDA*-1,5-*dicarboxamide* [(+)-(9c)].—The (+)-diacid chloride [(+)-(9b)] (230 mg) gave the *dicarboxamide* (123.4 mg), m.p. 309—310° (decomp.) (from MeOH), $[\alpha]_D^{25}$ +111.3 ± 6.4° (dioxan; *c* 0.071 85), $\nu_{max.}$ (Nujol) 3 330, 3 160, 1 735, and 1 615 cm^{-1} (Found: C, 69.45; H, 4.95; N, 9.15. $C_{18}H_{14}N_2O_3$ requires C, 70.6; H, 4.6; N, 9.15%).

(+)-1-*Carbamoyl*-11-*oxo-EDA Ethylene Dithioacetal*.—The (+)-11-carboxamide [(+)-(8c)] (199 mg) was treated according to the procedure for the preparation of (+)-(10). The oily residue was crystallized from ether to give *needles*, (216 mg), m.p. 278—279°, $[\alpha]_D^{24}$ +74.1 ± 3.1° ($CHCl_3$; *c* 0.374), $\nu_{max.}$ (Nujol) 3 410, 3 300, 1 686, 1 640, and 1 616 cm^{-1} (Found: C, 67.1; H, 5.3; N, 4.45; S, 18.7. $C_{19}H_{17}NOS_2$ requires C, 67.2; H, 5.05; N, 4.15; S, 18.9%).

(+)-*EDA*-1-*carboxamide* [(+)-(11c)].—The above ethylene dithioacetal (203 mg) was desulphurized by the procedure for (+)-(11a) to give *needles* (100 mg), m.p. 112—115°, $[\alpha]_D^{24}$ +121.5 ± 3.8° (MeOH; *c* 0.428), $\nu_{max.}$ (Nujol) 3 430, 3 160, and 1 648 cm^{-1} (Found: C, 81.7; H, 5.85; N, 5.55. $C_{17}H_{15}NO$ requires C, 81.9; H, 6.05; N, 5.6%).

(+)-*EDA*-1,5-*dicarboxamide* [(+)-(12c)].—This had m.p. >300° (from MeOH), *m/e* 292 (M^+), $[\alpha]_D^{24}$ +289.7 ± 18.9° (dioxan; *c* 0.175) (Found: C, 74.0; H, 5.3; N, 9.45. $C_{18}H_{16}N_2O_2$ requires C, 73.95; H, 5.5; N, 9.6%).

(+)-1-*Cyano*-11-*oxo-EDA* [(+)-(8d)].—A mixture of the (+)-amide [(+)-(8c)] (82.4 mg), thionyl chloride (0.5 ml), and dry tetrahydrofuran (3 ml) was heated under reflux for 5 h. The volatile materials were removed by distillation under reduced pressure. The oily residue was chromatographed on alumina (3 g; Merck grade 2) in benzene. The oily elute was crystallized from ether to give *prisms* (35 mg), m.p. 129—130°, $[\alpha]_D^{24}$ +170.8 ± 5.7° (MeOH; *c* 0.370), $\nu_{max.}$

(Nujol) 2 220 and 1 735 cm^{-1} (Found: C, 82.9; H, 4.55; N, 5.6. $C_{17}H_{11}NO$ requires C, 83.25; H, 4.5; N, 5.7%).

(+)-1,5-*Dicyano*-11-*oxo-EDA* [(+)-(9d)].—This had m.p. 195—196° (ether) (racemate m.p. 260—263°), $[\alpha]_D^{24}$ +259.5 ± 13.2° (dioxan, *c* 0.0370), $\nu_{max.}$ (Nujol) 2 225 and 1 743 cm^{-1} (Found: C, 79.85; H 3.55; N, 10.55. $C_{18}H_{10}N_2O$ requires C, 80.0; H, 3.75; N, 10.35%).

(+)-1-*Cyano-EDA* [(+)-(11d)].—This formed prisms, m.p. 97° (MeOH), *m/e* 231 (M^+), $[\alpha]_D^{24}$ +211.9 ± 8.5° (MeOH; *c* 0.295), $\nu_{max.}$ (Nujol) 2 225 and 745 cm^{-1} (Found: C, 89.45; H, 5.8; N, 6.0. $C_{17}H_{14}N$ requires C, 88.3; H, 5.65; N, 6.05%).

(+)-1,5-*Diamino*-11-*oxo-EDA* [(+)-(9h)].—A solution of the dicarboxylic acid chloride [(+)-(9b)] (359 mg) in dry tetrahydrofuran (5 ml) was added to a solution of NaN_3 (0.4 g) in water (3 ml) at 0° with stirring. The mixture was stirred for a further 1 h at 0°. Water (15 ml) was added. The crystals of the azide (11e) (351 mg) were collected by filtration, washed with water, and dried, m.p. 103—104° (decomp), $[\alpha]_D^{22}$ +419.2 ± 16.0° ($CHCl_3$, *c* 0.287), $\nu_{max.}$ (Nujol) 2 150 cm^{-1}. The azide (334 mg), t-butyl alcohol (10 ml), and triethylamine (2 ml) were heated under reflux for 30 min. Crystals (232 mg) were collected by filtration, washed with ethanol, and dried, m.p. >300°, $\nu_{max.}$ (Nujol) 1 725 cm^{-1}. This carbamate (11 g) could not be dissolved in any solvent.

A mixture of the carbamate (197 mg) and concentrated HCl (10 ml) was heated under reflux for 7 h and then treated with charcoal. The filtrate was concentrated to 1 ml by distillation under reduced pressure. The crystals were collected by filtration, washed with ethanol, and dried. The crude salt (107 mg) was added to aqueous K_2CO_3 and the mixture was extracted with methylene chloride. The solution was dried (K_2CO_3) and the solvent was removed by distillation under reduced pressure. The oily residue was dissolved in ethyl acetate and insoluble materials were removed by filtration. The solvent was removed and the residue was dissolved in methanol. Insoluble materials were again removed by filtration. Two drops of concentrated HCl were added. Crystals of the diamine were collected by filtration, m.p. >300°, $[\alpha]_D^{26}$ +89.3 ± 6.0° (MeOH; *c* 0.214), $\nu_{max.}$ (Nujol) 3 520, 3 410, and 1 743 cm^{-1} (Found: C, 55.25; H, 5.5; Cl, 19.45; N, 7.75. $C_{16}H_{16}Cl_2N_2O,2H_2O$ requires C, 55.5; H, 5.35; Cl, 18.9; N, 7.45%).

(+)-1-*Amino*-11-*oxo-EDA* [(+)-(8h)].—The (+)-acid chloride [(+)-(8b)] (840 mg) was treated according to the procedure cited above. However, the carbamate (10 g) could not be reacted with concentrated HCl. The carbamate (229 mg) was stirred in a solution of HCl in glacial AcOH (20 ml) at room temperature for 1 h. From the clear solution, the volatile materials were removed by distillation under reduced pressure. The crystalline residue was recrystallized from ethanol. The crystals were shaken with a mixture of aqueous KOH and methylene chloride. The organic phase was separated and aqueous phase was extracted with methylene chloride. The combined organic phases were dried (K_2CO_3) and the solvent was removed by distillation under reduced pressure. The *residue* was crystallized from ethanol, m.p. 257—259° (decomp.), *m/e* 235 (M^+), $[\alpha]_D^{25}$ +94.4 ± 3.2° ($CHCl_3$, *c* 0.413), $\nu_{max.}$ (Nujol) 3 280 and 1 730 cm^{-1} (Found: C, 78.4; H, 5.0; N, 5.55. $C_{16}H_{13}NO,0.5H_2O$ requires C, 78.65; H, 5.8; N, 5.7%).

(+)-1,5-*Dihydroxymethyl*-11-*oxo-EDA* [(+)-9(j)].—A mixture of the (+)-11-oxo-ester [(+)-(9i)] (123 mg), ethylene glycol (0.5 ml), toluene-*p*-sulphonic acid (25 ml), and dry toluene (20 ml) was heated under reflux for 10 h, while the solvent was distilled off little by little. Sodium methoxide and then water were added and the organic phase was separated. The aqueous phase was extracted with ether. The combined organic phases were washed with water, dried (Na_2SO_4), and concentrated to dryness. The oily residue was crystallized on standing at room temperature for 2 months, m.p. 140—142°, $\nu_{max.}$ (Nujol) 1 719 and 1 068 cm^{-1} (Found: C, 69.2; H, 5.45. $C_{22}H_{20}O_6$ requires C, 69.45; H, 5.3%).

A solution of the acetal (120 mg) in dry tetrahydrofuran (8 ml) was added to a slurry of excess of $LiAlH_4$ in tetrahydrofuran (2 ml) at 0° with stirring under nitrogen over 10 min. The temperature was raised gradually to room and then reflux temperature. The mixture was heated for a further 2 h. Excess of $LiAlH_4$ was decomposed by addition of methanol–ether and then dilute HCl under cooling in ice. The organic phase was separated and the aqueous phase was extracted with ether. The combined organic phases were washed with water and dried (Na_2SO_4). The solvent was removed by distillation under reduced pressure. The residue was chromatographed on thin silica gel plate [Merck GF; benzene–ethyl acetate (2 : 1)]. The elute could not be crystallized.

(+)-1-*Hydroxymethyl*-11-*oxo-EDA* [(+)-(8j)].—The (+)-11-oxo-ester [(+)-(8i)] (420 mg) was treated by the same procedure. The ethylene acetal could not be crystallized and used for the reduction. The oily residue was chromatographed on thin silica gel plates [Merck GF; benzene–ethyl acetate (1 : 1)]. The fraction with the largest R_F value was crystallized from benzene to give *needles*, m.p. 108—110°, $[\alpha]_D^{25}$ +55.7 ± 1.4° (MeOH; *c* 0.714), $\nu_{max.}$ (Nujol) 3 320 and 1 725 cm^{-1} (Found: C, 81.55; H, 5.65. $C_{17}H_{14}O_2$ requires C, 81.6; H, 5.65%).

(+)-1-*Hydroxymethyl*-11-*oxo-EDA Ethylene Dithioacetal.*—The (+)-11-oxo-alcohol [(+)-(8j)] (80 mg) was treated in the same manner as for (+)-(8a), m.p. 195—197° (from benzene), $[\alpha]_D^{23}$ +31.7 ± 2.0° ($CHCl_3$; *c* 0.356) (Found: C, 69.7; H, 5.4; S, 19.35. $C_{19}H_{18}S_2O$ requires C, 69.9; H, 5.55; S, 19.65%).

(+)-1-*Hydroxymethyl-EDA* [(+)-(11j)].—The (+)-ethylene dithioacetal (25 mg) was desulphurized as for (+)-(11a). The oily residue was chromatographed on thin silica gel plates [Merck GF; benzene–ethyl acetate (4 : 1)] but could not be crystallized (Found: C, 86.35; H, 6.95. $C_{17}H_{16}O$ requires C, 86.4; H, 6.8%).

U.v. Spectra of Tetralin Derivatives.—Methyl tetralin-1-carboxylate (14b), $\lambda_{max.}$ (n-heptane) 258 (ε 1 760), 235.5 (8 370), and 205 nm (41 300); tetralin-1-carboxamide (14d), $\lambda_{max.}$ (EtOH) 275.5 (ε 903), 229sh (4 050), and 200.5 nm (38 200); 1-cyanotetralin (14e), $\lambda_{max.}$ (n-heptane) 290 (ε 2 190), 286 (16 00), 280 (1 880), 273sh (1 110), 239 (9 500), 233 (10 500), 229sh (8 930), and 203 nm (50 600); 1-hydroxytetralin (14f), $\lambda_{max.}$ (n-heptane) 277 (ε 633), 272sh (416), 268 (454), 265sh (406), 215 (8 960), 202 (43 200), and 198 nm (43 700); 1-aminotetralin (14g), $\lambda_{max.}$ (EtOH) 286 (ε 1 250), 238.5 (10 600), and 205 nm (53 300).

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