

[JOINT CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF NEW YORK UNIVERSITY, NEW YORK 53, N. Y., AND OF STANFORD UNIVERSITY, STANFORD, CALIF.]

## Inherently Dissymmetric Chromophores and Circular Dichroism. II<sup>1, 2</sup>

BY KURT MISLOW,<sup>3a</sup> E. BUNNENBERG, RUTH RECORDS, KEITH WELLMAN<sup>3b</sup> AND CARL DJERASSI

RECEIVED NOVEMBER 28, 1962

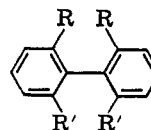
In a continued investigation of the ultraviolet circular dichroism (C.D.) curves of optically active substances possessing inherently dissymmetric chromophores, the previously discussed<sup>1,2,8</sup> relationship between ultraviolet absorption spectra, optical rotatory dispersion (O.R.D.) and C.D. curves has now been extended to various representatives of bridged and unbridged biphenyls and binaphthyls. In addition to confirming the earlier O.R.D. results, this work serves to accent the relative advantages of C.D. and O.R.D. measurements in a class of complex chromophores.

In a preliminary survey,<sup>1</sup> we reported that circular dichroism (C.D.) curves of twisted biphenyls are extremely useful in the identification of the electronic transitions which are responsible for the individual Cotton effects and which give rise to the associated optical rotatory dispersion (O.R.D.) curves. The intensities of the C.D. curves were seen to parallel both the high extinctions in the absorption spectra

The marked reduction of overlapping tails in the C.D., as compared to the O.R.D. curves, was found to be especially significant in that it permitted identification of weakly optically active transitions whose Cotton effects had previously been unsuspected because they had been completely masked by the intense tailings of high amplitude Cotton effects centered at shorter wave lengths. As a result of these preliminary ob-

TABLE I

DATA ON BIARYLS I-XIV OF FORMULA TYPE



Circular dichroism data

No.	R	R'	Config.	Solvent	Circular dichroism data
I	NO <sub>2</sub>	CH <sub>3</sub>	(S)	Dioxane	[θ] <sub>367</sub> -2000, [θ] <sub>350</sub> -2300, [θ] <sub>326</sub> -1300, [θ] <sub>298</sub> -9200, [θ] <sub>288</sub> -6700, [θ] <sub>215</sub> -3200, [θ] <sub>251</sub> +16,000, [θ] <sub>239</sub> +8700 (c 0.50-0.01)
II	NO <sub>2</sub>	CH <sub>2</sub> Br	(R)	Dioxane	[θ] <sub>430</sub> +150, [θ] <sub>360</sub> +5160, [θ] <sub>340</sub> +6840, [θ] <sub>316</sub> +2280, [θ] <sub>300</sub> +8500, [θ] <sub>290</sub> +9500, [θ] <sub>250</sub> +13,300, [θ] <sub>275</sub> 0.00, [θ] <sub>255</sub> -30,400 (c 0.7-0.028)
III	NO <sub>2</sub>	COOH	(R)	Dioxane	[θ] <sub>430</sub> 0.00, [θ] <sub>370</sub> +5200, [θ] <sub>330</sub> +10,700, [θ] <sub>310</sub> +5700, [θ] <sub>290</sub> +4700, [θ] <sub>215</sub> 0.00 (c 0.9-0.018)
IV	NO <sub>2</sub>	COOCH <sub>3</sub>	(S)	Dioxane	[θ] <sub>420</sub> 0.00, [θ] <sub>310</sub> -4900, [θ] <sub>330</sub> -10,200, [θ] <sub>310</sub> -7700, [θ] <sub>290</sub> -5500, [θ] <sub>270</sub> 0.00 (c 1.0-0.1)
V	NO <sub>2</sub>	CH <sub>2</sub> OH	(S)	Dioxane	[θ] <sub>410</sub> 0.00, [θ] <sub>345</sub> -5300, [θ] <sub>320</sub> -2350, [θ] <sub>300-290</sub> -8820, [θ] <sub>215</sub> -4420 (c 0.32-0.013)
VI	CH <sub>3</sub>	Br	(R)	Isooctane	[θ] <sub>295-288</sub> -425, [θ] <sub>219</sub> +2000, [θ] <sub>215</sub> +1400, [θ] <sub>211</sub> +2420, [θ] <sub>250-245</sub> -1800, [θ] <sub>235</sub> -5600, [θ] <sub>228</sub> -4200 (c 0.2-0.02)
VII	CH <sub>3</sub>	Cl	(R)	Isooctane	[θ] <sub>300-290</sub> 0.00, [θ] <sub>219</sub> +2200, [θ] <sub>215</sub> +1500, [θ] <sub>270</sub> +2800, [θ] <sub>266-263</sub> +2000, [θ] <sub>248</sub> 0.00, [θ] <sub>231</sub> -7700, [θ] <sub>277</sub> -3100 (c 0.2-0.04)
VIII	CH <sub>3</sub>	I	(S)	Isooctane	[θ] <sub>318</sub> 0.00, [θ] <sub>258</sub> -900, [θ] <sub>281</sub> -4300, [θ] <sub>219</sub> -3000, [θ] <sub>212</sub> -4000, [θ] <sub>266</sub> -2500, [θ] <sub>253</sub> -6000, [θ] <sub>239</sub> +38,000, [θ] <sub>236-234</sub> +32,500 (c 1.0-0.02)
IX	CH <sub>3</sub>	CONH <sub>2</sub>	(R)	Dioxane	[θ] <sub>300-290</sub> 0.00, [θ] <sub>250</sub> +1500, [θ] <sub>255</sub> +31,000, [θ] <sub>250</sub> +33,000 (c 0.04-0.01)
X	CH <sub>3</sub>	COOCH <sub>3</sub>	(R)	Dioxane	[θ] <sub>320-310</sub> -1400, [θ] <sub>295</sub> -2400, [θ] <sub>290-280</sub> 0.00, [θ] <sub>260</sub> -7000, [θ] <sub>252</sub> 0.00 (c 0.054-0.014)
XI	Cl	COOH	(S)	Dioxane	[θ] <sub>320</sub> 0.00, [θ] <sub>305</sub> -770, [θ] <sub>300-290</sub> 0.00, [θ] <sub>215</sub> +2000, [θ] <sub>251</sub> -15,400 (c 0.2-0.02)
XII	Cl	CONH <sub>2</sub>	(S)	Dioxane	[θ] <sub>300-290</sub> 0.00, [θ] <sub>253</sub> -32,000, [θ] <sub>245</sub> -28,000, (c 0.04-0.005)
XIII	NH <sub>2</sub>	CH <sub>3</sub>	(R)	Dioxane	[θ] <sub>330</sub> -1200, [θ] <sub>315</sub> -4820, [θ] <sub>305</sub> -12,000, [θ] <sub>256</sub> +19,300, [θ] <sub>215</sub> 7220, [θ] <sub>230</sub> +5800, [θ] <sub>255</sub> +14,400 (c 0.044-0.011)
XIV	NH <sub>3</sub> <sup>+</sup>	CH <sub>3</sub>	(R)	0.1 N HCl	No deflections were obsd. from 350 to 245 mμ. The init. concn. was diluted 1:5. Subsequent 1:2 dilut. were made as required.

and the high amplitudes in the O.R.D. curves: all three phenomena are characteristic of molecules which contain inherently dissymmetric chromophores. The shapes of the C.D. curves are in excellent accord with those of the absorption curves, a correspondence which is predicted by theory. The signs of the C.D. curves were found to correspond to the signs of the related O.R.D. curves, which had previously been shown to reflect the chirality of the chromophore.<sup>4</sup>

(1) Part I, E. Bunnenberg, C. Djerassi, K. Mislow and A. Moscovitz, *J. Am. Chem. Soc.*, **84**, 2823, 5003 (1962).

(2) The present paper represents part LXXX of the series on "Optical Rotatory Dispersion Studies" from the Stanford Laboratories; for part LXXIX, see C. Djerassi, H. Wolf and E. Bunnenberg, *J. Am. Chem. Soc.*, **85**, 324 (1963). The work at Stanford has been supported by the National Science Foundation (Grant No. G-19905).

(3) (a) Fellow of the Alfred P. Sloan Foundation. (b) National Institutes of Health Postdoctoral Research Fellow, 1962-1963.

servations it became immediately obvious that the presence of weakly optically active transitions might also have gone undetected in our previous O.R.D. study of other related biaryls,<sup>5</sup> and an investigation of the C.D. curves of these substances seemed to be indicated on these grounds alone. In addition, the subject of dissymmetric chromophores is of sufficient theoretical interest so that a broadening of the experimental basis of our earlier conclusions<sup>1</sup> appears to be more than justified.

### Discussion of Results

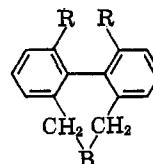
**Chromophoric Groups.**—Our findings are reported in Tables I-IV and Fig. 1-15. As in the preceding

(4) K. Mislow, *Ann. N. Y. Acad. Sci.*, **93**, 457 (1962), and references cited therein.

(5) K. Mislow, M. A. W. Glass, R. E. O'Brien, P. Rutkin, D. H. Steinberg, J. Weiss and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1455 (1962).

TABLE II

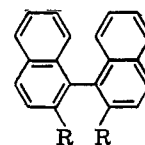
DATA ON BIARYLS XV-XXV OF FORMULA TYPE



No.	R	B	Config.	Solvent	Circular dichroism data
XV	NO <sub>2</sub>	CO	(S)	Dioxane	[ $\theta$ ] <sub>400</sub> 0.00, [ $\theta$ ] <sub>338</sub> +44,900, [ $\theta$ ] <sub>297</sub> -55,200, [ $\theta$ ] <sub>278-268</sub> 0.00, [ $\theta$ ] <sub>253</sub> -30,900 ( <i>c</i> 0.05-0.005)
XVI	NO <sub>2</sub>	CHOH	(S)	Dioxane	[ $\theta$ ] <sub>420</sub> +1000, [ $\theta$ ] <sub>333</sub> +48,000, [ $\theta$ ] <sub>300-288</sub> +8000, [ $\theta$ ] <sub>258</sub> -38,000, [ $\theta$ ] <sub>240</sub> -10,000 ( <i>c</i> 0.1-0.05)
XVII	NO <sub>2</sub>	N <sup>+</sup> [(CH <sub>2</sub> ) <sub>5</sub> ]Br <sup>-</sup>	(R)	Water	[ $\theta$ ] <sub>420</sub> 0.00, [ $\theta$ ] <sub>368</sub> -19,000, [ $\theta$ ] <sub>327</sub> -56,000, [ $\theta$ ] <sub>300</sub> -15,000, [ $\theta$ ] <sub>288</sub> -9000, [ $\theta$ ] <sub>262</sub> +82,000, [ $\theta$ ] <sub>228</sub> -16,500 ( <i>c</i> 0.13-0.0054)
XVIII	NO <sub>2</sub>	C(CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	(R)	Dioxane	[ $\theta$ ] <sub>402</sub> 0.00, [ $\theta$ ] <sub>370</sub> -15,000, [ $\theta$ ] <sub>330</sub> -57,000, [ $\theta$ ] <sub>300</sub> -8000, [ $\theta$ ] <sub>290</sub> -16,000, [ $\theta$ ] <sub>257</sub> +107,000 ( <i>c</i> 0.05-0.01)
XIX	NH <sub>2</sub>	C(CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	(R)	Dioxane	[ $\theta$ ] <sub>350</sub> 0.00, [ $\theta$ ] <sub>330</sub> -2380, [ $\theta$ ] <sub>320</sub> -11,800, [ $\theta$ ] <sub>302</sub> +19,800, [ $\theta$ ] <sub>282</sub> -11,900, [ $\theta$ ] <sub>252</sub> 110,000 ( <i>c</i> 0.057-0.011)
XX	NH <sub>3</sub> <sup>+</sup>	C(CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	(R)	0.1 N HCl	No deflections were obsd. from 400 to 245 m $\mu$ . The init. concn., 1.15 g./l., was diluted 1:5. Subsequent 1:2 diln. were made as required.
XXI	CH <sub>3</sub>	C(CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	(R)	Dioxane	[ $\theta$ ] <sub>294</sub> 0.00, [ $\theta$ ] <sub>284</sub> +2700, [ $\theta$ ] <sub>279-276</sub> -1800, [ $\theta$ ] <sub>271</sub> -4600, [ $\theta$ ] <sub>268</sub> 0.00, [ $\theta$ ] <sub>245</sub> +128,000 ( <i>c</i> 0.1-0.005)
XXII	CH <sub>3</sub>	CHOH	(S)	Isoöctane	[ $\theta$ ] <sub>300</sub> 0.00, [ $\theta$ ] <sub>286</sub> -8500, [ $\theta$ ] <sub>271</sub> +4100, [ $\theta$ ] <sub>242</sub> -11,800 ( <i>c</i> 0.2-0.002)
XXIII	Cl	C(CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	(R)	Isoöctane	[ $\theta$ ] <sub>300</sub> 0.00, [ $\theta$ ] <sub>291</sub> +10,500, [ $\theta$ ] <sub>275</sub> -17,200, [ $\theta$ ] <sub>245</sub> +83,100, [ $\theta$ ] <sub>233</sub> +70,600, [ $\theta$ ] <sub>224</sub> +121,000 ( <i>c</i> 0.25-0.005)
XXIV	Cl	N <sup>+</sup> [(CH <sub>2</sub> ) <sub>5</sub> ]Br <sup>-</sup>	(R)	Water	[ $\theta$ ] <sub>300</sub> 0.00, [ $\theta$ ] <sub>293</sub> +3680, [ $\theta$ ] <sub>275</sub> -9200, [ $\theta$ ] <sub>245</sub> +90,200, [ $\theta$ ] <sub>241</sub> +81,000, [ $\theta$ ] <sub>226</sub> +184,000, [ $\theta$ ] <sub>222</sub> +153,000 ( <i>c</i> 0.05-0.005)
XXV	CH <sub>3</sub>	...	(R)	Isoöctane	[ $\theta$ ] <sub>280</sub> 0.00, [ $\theta$ ] <sub>262</sub> +56,300, [ $\theta$ ] <sub>243</sub> 0.00, [ $\theta$ ] <sub>235</sub> -48,300 ( <i>c</i> 0.0016)

TABLE III

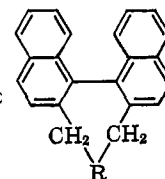
DATA ON BIARYLS XXVI-XXXI OF FORMULA TYPE



No.	R	Config.	Solvent	Circular dichroism data
XXVI	CHOH	(R)	Dioxane	[ $\theta$ ] <sub>352</sub> +4000, [ $\theta$ ] <sub>313</sub> +4500, [ $\theta$ ] <sub>284</sub> +41,300, [ $\theta$ ] <sub>268</sub> +9000, [ $\theta$ ] <sub>235</sub> -38,000, [ $\theta$ ] <sub>220</sub> -241,000 ( <i>c</i> 0.02-0.004)
XXVII	CH <sub>3</sub>	(S)	Dioxane	[ $\theta$ ] <sub>300</sub> 0.00, [ $\theta$ ] <sub>285</sub> -15,700, [ $\theta$ ] <sub>260</sub> +23,500, [ $\theta$ ] <sub>250</sub> +33,000, [ $\theta$ ] <sub>245</sub> +78,500 ( <i>c</i> 0.0044)
XXVIII	COOH	(S)	Dioxane	[ $\theta$ ] <sub>342</sub> 0.00, [ $\theta$ ] <sub>322</sub> -11,000, [ $\theta$ ] <sub>313</sub> -8500, [ $\theta$ ] <sub>295</sub> -35,500, [ $\theta$ ] <sub>290</sub> -45,600, [ $\theta$ ] <sub>285</sub> -53,300, [ $\theta$ ] <sub>260</sub> 0.00 ( <i>c</i> 0.04-0.004)
XXIX	COOCH <sub>3</sub>	(S)	Dioxane	[ $\theta$ ] <sub>368</sub> +6000, [ $\theta$ ] <sub>326</sub> -11,800, [ $\theta$ ] <sub>305</sub> -5000, [ $\theta$ ] <sub>288</sub> -70,700, [ $\theta$ ] <sub>245</sub> +524,000, [ $\theta$ ] <sub>240</sub> +460,000 ( <i>c</i> 0.1-0.004)
XXX	CONH <sub>2</sub>	(S)	Dioxane	[ $\theta$ ] <sub>310</sub> 0.00, [ $\theta$ ] <sub>287</sub> -42,400, [ $\theta$ ] <sub>272</sub> -30,000, [ $\theta$ ] <sub>260</sub> -22,500, [ $\theta$ ] <sub>255</sub> 0.00 ( <i>c</i> 0.0074-0.0019)
XXXI	CH <sub>2</sub> Br	(S)	Dioxane	[ $\theta$ ] <sub>350</sub> 0.00, [ $\theta$ ] <sub>305</sub> -5750, [ $\theta$ ] <sub>289</sub> -46,000, [ $\theta$ ] <sub>269</sub> 0.00 ( <i>c</i> 0.47-0.0076)

TABLE IV

DATA ON BIARYLS XXXII-XXXV OF FORMULA TYPE



No.	R	Config.	Solvent	Circular dichroism data
XXXII	CO	(R)	Isoöctane	[ $\theta$ ] <sub>340</sub> 0.00, [ $\theta$ ] <sub>333</sub> +10,000, [ $\theta$ ] <sub>327</sub> +95,000, [ $\theta$ ] <sub>323</sub> +60,000, [ $\theta$ ] <sub>318</sub> +100,000, [ $\theta$ ] <sub>315</sub> +95,000, [ $\theta$ ] <sub>300</sub> +155,000, [ $\theta$ ] <sub>293</sub> +105,000, [ $\theta$ ] <sub>282</sub> +85,000, [ $\theta$ ] <sub>265</sub> -125,000, [ $\theta$ ] <sub>250</sub> -45,000, [ $\theta$ ] <sub>240</sub> -42,000, [ $\theta$ ] <sub>232</sub> -1,210,000, [ $\theta$ ] <sub>228</sub> -640,000 ( <i>c</i> 0.022-0.0009)
XXXIII	CHOH	(R)	Dioxane	[ $\theta$ ] <sub>340</sub> 0.00, [ $\theta$ ] <sub>330</sub> +7000, [ $\theta$ ] <sub>305</sub> +54,000, [ $\theta$ ] <sub>280</sub> 0.00, [ $\theta$ ] <sub>267</sub> -128,000, [ $\theta$ ] <sub>252</sub> 0.00 ( <i>c</i> 0.006-0.0012)
XXXIV	C(CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	(S)	Dioxane	[ $\theta$ ] <sub>340</sub> 0.00, [ $\theta$ ] <sub>275</sub> -41,000, [ $\theta$ ] <sub>305</sub> -69,000, [ $\theta$ ] <sub>285</sub> -35,000, [ $\theta$ ] <sub>265</sub> +103,000, [ $\theta$ ] <sub>260</sub> +96,000 ( <i>c</i> 0.016-0.079)
XXXV	O	(S)	Dioxane	[ $\theta$ ] <sub>340</sub> +3300, [ $\theta$ ] <sub>364</sub> +6600, [ $\theta$ ] <sub>305</sub> -51,000, [ $\theta$ ] <sub>263</sub> +144,000, [ $\theta$ ] <sub>234-231</sub> +133,000, [ $\theta$ ] <sub>232</sub> -145,000, [ $\theta$ ] <sub>228</sub> 0.00 ( <i>c</i> 0.02-0.0004)

O.R.D. study,<sup>5</sup> chromophorically related substances were found to exhibit very similar rotatory properties which in the present case are reflected in the very similar C.D. curves for each such group. This behavior is expected as a matter of course from the similarity of the relevant electronic transitions.

For example, the C.D. curves of the unbridged 2,2'-dinitrobiphenyls display common features which are in an obvious way related to their absorption characteristics. Figure 1 shows C.D. and absorption curves of one such compound, (S)-6,6'-dinitro-2,2'-dimethylbiphenyl (I). The short-wave length posi-

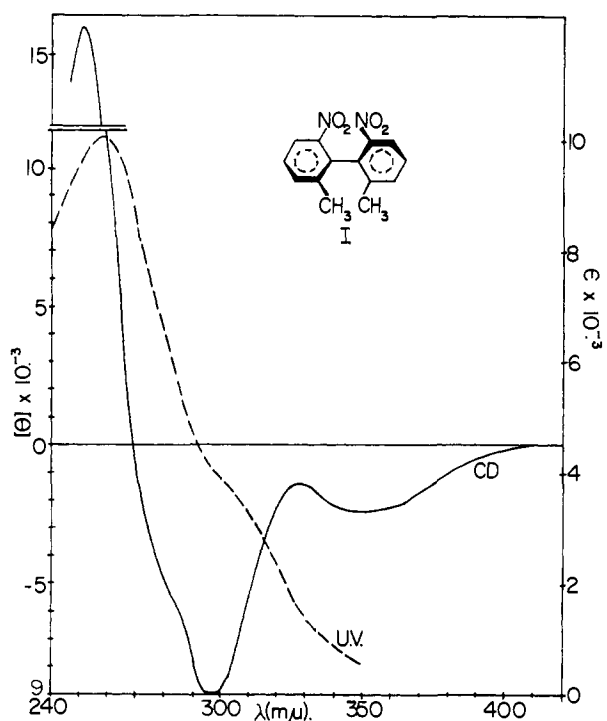


Fig. 1.

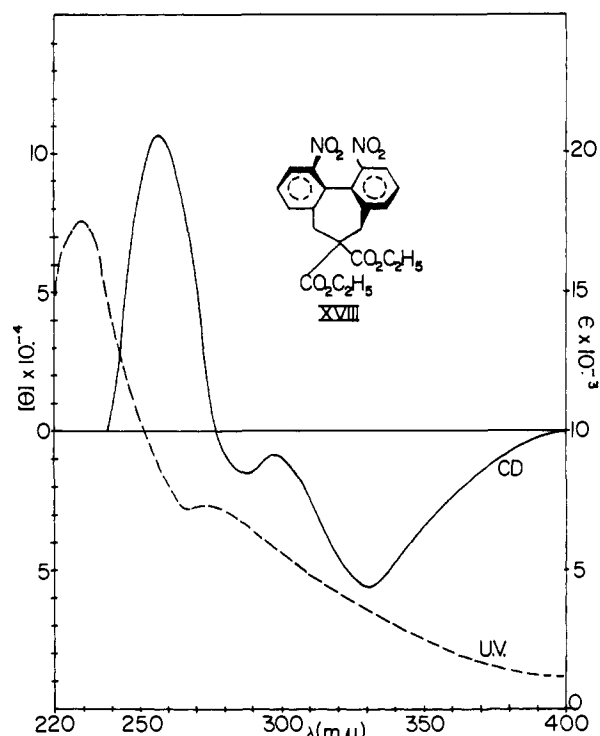


Fig. 3.

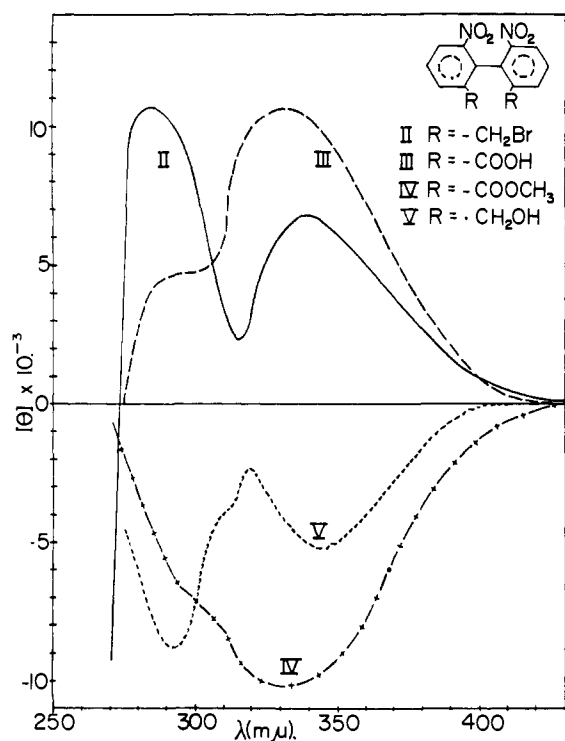


Fig. 2.

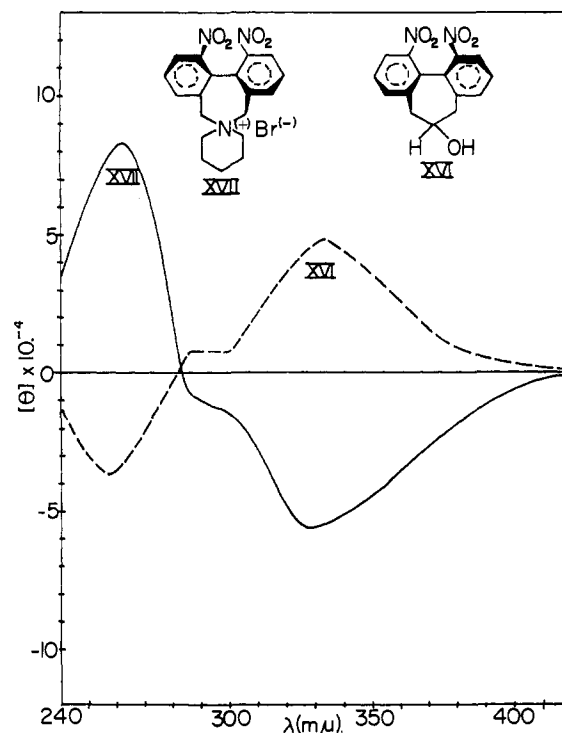


Fig. 4.

tive C.D. maximum<sup>6</sup> at 251 m $\mu$  corresponds to the absorption maximum at 260 m $\mu$ , and the negative C.D. maximum<sup>6</sup> at 298 m $\mu$  corresponds to the inflection at ca. 310 m $\mu$ . The long-wave length negative C.D. maximum near 350 m $\mu$  is associated with a transition which is not apparent in the ultraviolet spectrum. These signed features are characteristic of the (*S*)-configuration and are shared by the chromophorically related II-V which have in common the signed (nega-

(6) The maxima of circular dichroism curves are signed, and it becomes necessary to speak of positive and negative maxima. The close relationship of circular dichroism maxima to necessarily unsigned transitions in the absorption spectra makes it misleading to speak of negative maxima as "minima."

tive for the (*S*)-configuration and positive for the (*R*)-configuration) long-wave length C.D. maxima near 300 and 340 m $\mu$  (Fig. 2).

It is instructive to recall the previously discussed O.R.D. results in the same series.<sup>5</sup> It had then been found that the 2,2'-dinitrophenyls exhibit two Cotton effects of opposite sign centered near 260 and 330 m $\mu$ , respectively, and it had been concluded that the positive 330 m $\mu$  Cotton effect corresponded to the (*R*)-configuration. The present C.D. results completely support the earlier conclusions. It is particularly noteworthy (a) that the masked nitrobenzene

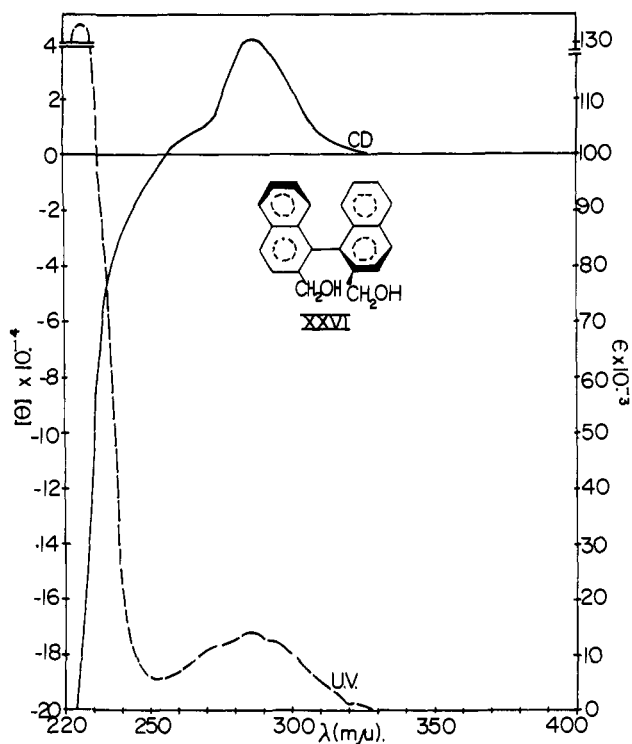


Fig. 5.

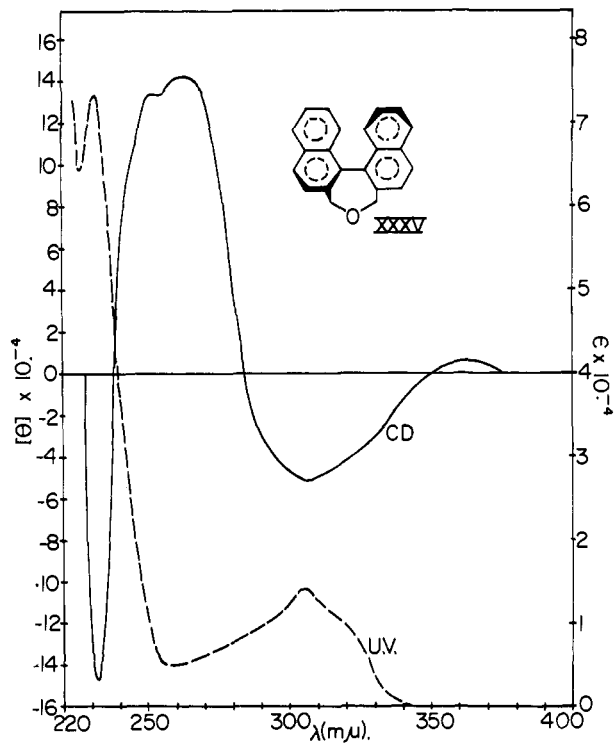


Fig. 7.

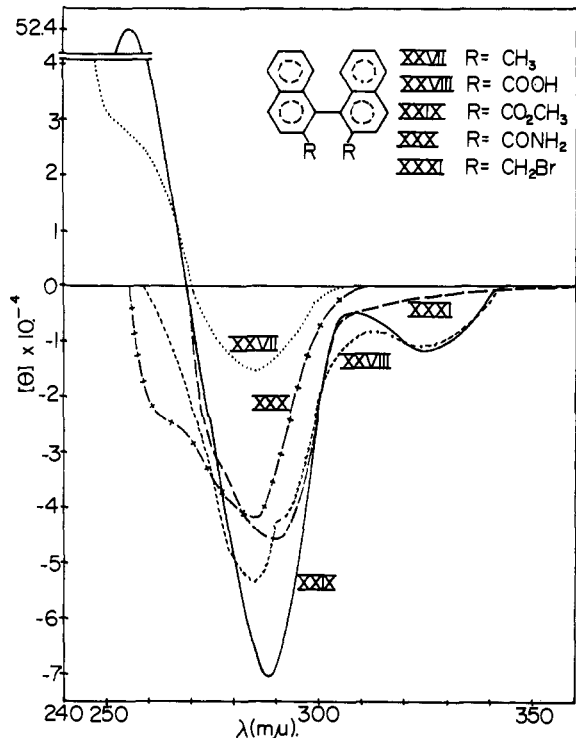


Fig. 6.

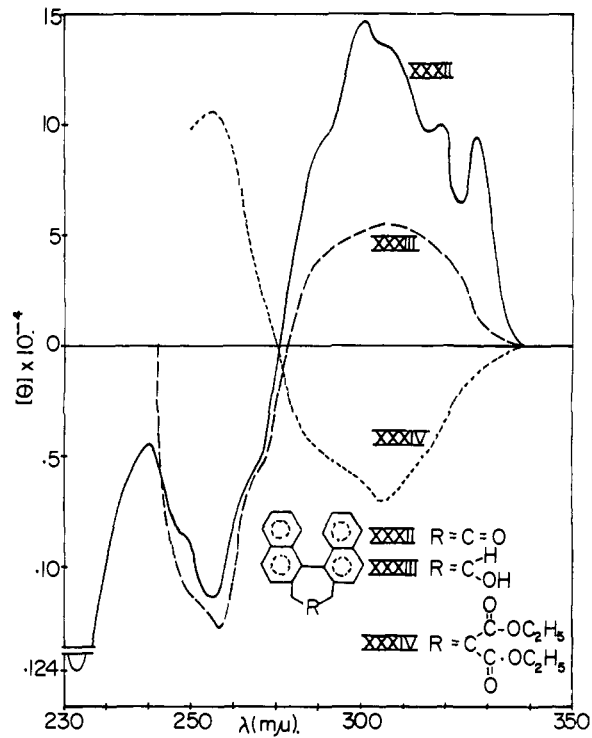


Fig. 8.

transition near 340  $m\mu$  has now been clearly revealed both by C.D. and by O.R.D., and (b) that the transition near 300  $m\mu$  has been shown to be optically active by C.D. measurement, a fact which had eluded us in the earlier experiments where the tails of neighboring Cotton effects had obscured the small Cotton effect associated with this transition.

In much the same way, the C.D. curves of bridged 2,2'-dinitrobiphenyls, while confirmatory of earlier O.R.D. results,<sup>5</sup> disclose heretofore unsuspected features. Figure 3 shows C.D. and absorption curves of the (*R*)-diester XVIII. The short-wave length posi-

tive C.D. maximum at 257  $m\mu$  corresponds to one of the absorption maxima below 280  $m\mu$ , and one of the negative C.D. maxima near 290 and 330  $m\mu$  corresponds to the inflection near 310  $m\mu$ . These features are characteristic of the (*R*)-configuration and are shared by the chromophorically related compounds XVI and XVII (Fig. 4). Our earlier conclusions<sup>5</sup> are therefore supported: for the bridged 2,2'-dinitrobiphenyls, two oppositely signed Cotton effects are centered near 260 and 330  $m\mu$ , and a negative 330  $m\mu$  Cotton effect signals the (*R*)-configuration. In agreement with the earlier conclusions, the intensity

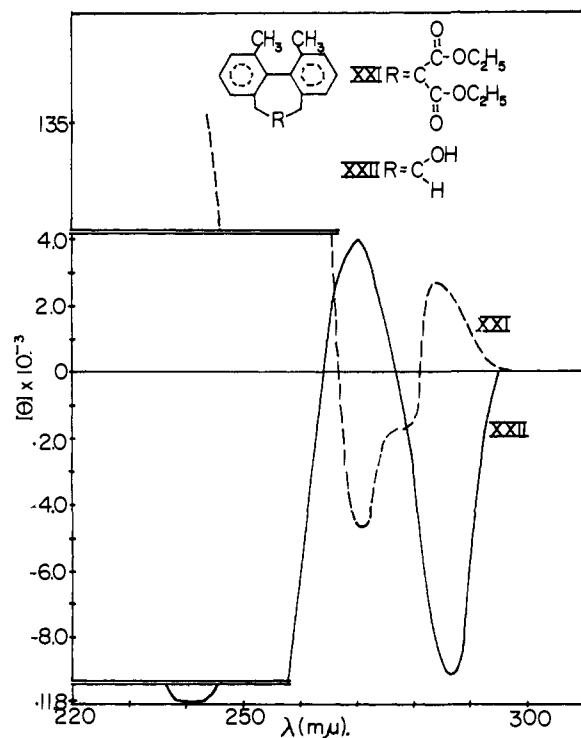


Fig. 9.

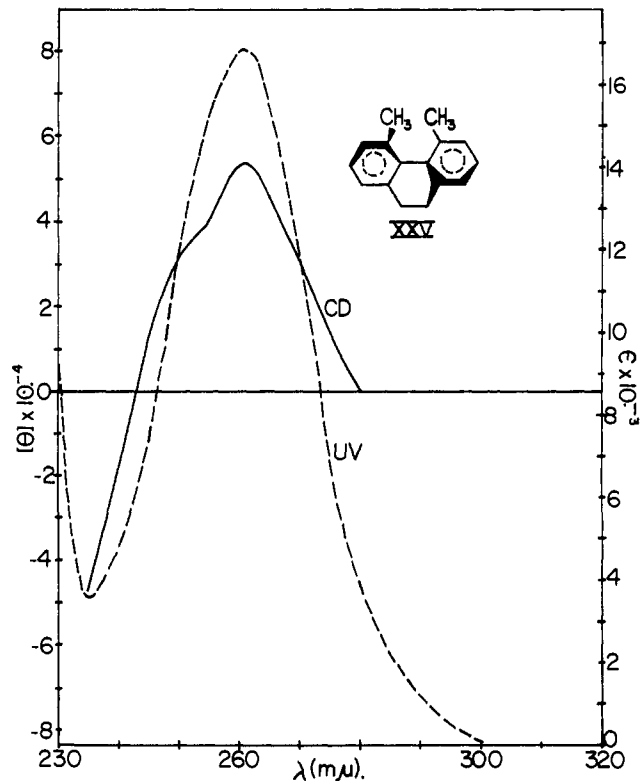


Fig. 11.

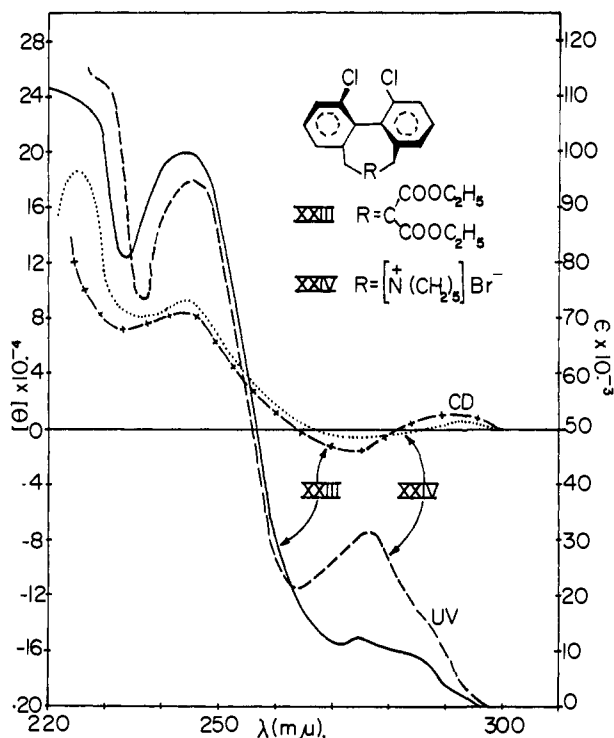


Fig. 10.

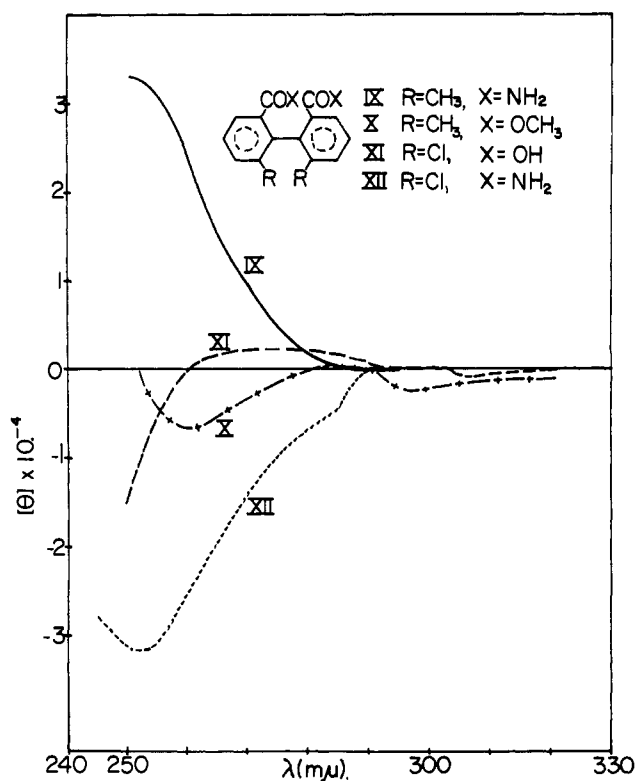


Fig. 12.

of both Cotton effects is significantly enhanced by bridging but there appears to be no marked red-shift. It is remarkable how sharply the weak transition near 290  $m\mu$ , hidden in both absorption and O.R.D. curves, has now been brought out in the C.D. curves.

In the 1,1'-binaphthyls, the correspondence between earlier O.R.D. data<sup>5</sup> and the present C.D. results is also satisfactory. The unbridged binaphthyls have absorption maxima at 285 and *ca.* 230  $m\mu$ ,<sup>5</sup> and, as exemplified by compound XXVI (Fig. 5), the C.D. curves are signed reflections of these spectral characteristics. A positive 285  $m\mu$  Cotton effect corresponds to the (*R*)-configuration in this and related compounds

XXVII-XXXI (Fig. 6), as had been concluded earlier on the basis of O.R.D. data alone. The 2,2'-bridged 1,1'-binaphthyls XXXII-XXXV have in common oppositely signed C.D. maxima at *ca.* 270 and 310  $m\mu$  (Fig. 7 and 8). These correspond to the oppositely signed O.R.D. curves centered near 265  $m\mu$  and near 300  $m\mu$ , respectively, as had been observed before.<sup>5</sup> Furthermore, in harmony with the earlier conclusion,<sup>5</sup> a positive 306  $m\mu$  Cotton effect corresponds to the (*R*)-

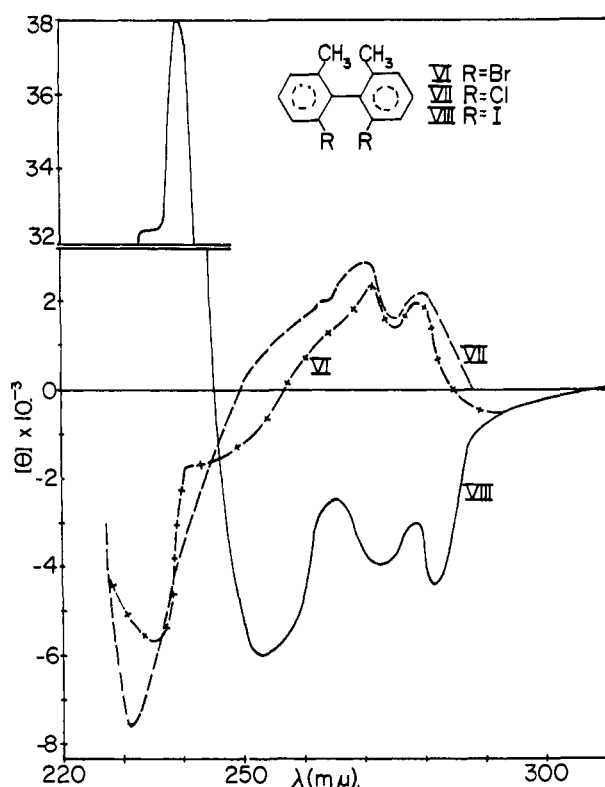


Fig. 13.

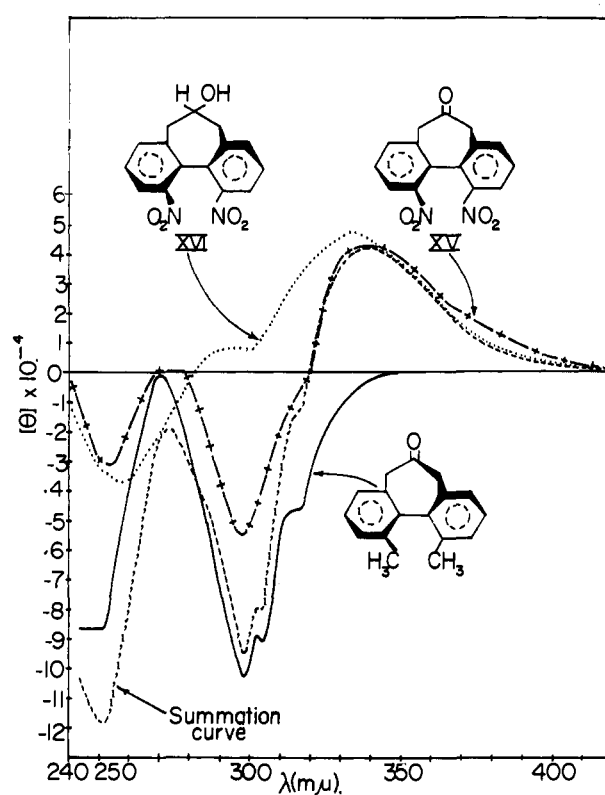


Fig. 14.

configuration. In the case of compound XXXV, it was even possible to ascertain that the 230 m $\mu$  transition is also strongly optically active.

Although the C.D. curve of the binaphthyl ketone XXXII bears a general resemblance to the curves of the other 2,2'-bridged 1,1'-binaphthyls, the greater complexity in the region above 320 m $\mu$ , as well as the greater intensity of the long-wave length maximum, reveal the operation of a second effect. We believe that the intensified carbonyl  $n \rightarrow \pi^*$ -transition which characterizes  $\beta, \gamma$ -benzo-ketones having the geometry of XXXII may be held to account for these departures from the norm.

The bridged 2,2'-dimethyl- and 2,2'-dihalobiphenyls XXI-XXII and XXIII-XXIV, respectively, show a C.D. pattern (Fig. 9 and 10) which is characteristic of this group of compounds and which, as expected, resembles the C.D. behavior of the previously discussed bridged dimethylbiphenyls.<sup>1</sup> In the wave length region between 270 and 300 m $\mu$ , two relatively low-intensity, oppositely signed C.D. maxima are displayed by all four compounds. A positive maximum at longer wave lengths signals the (*R*)-configuration; in this respect the present C.D. data merely serve to confirm the conclusions drawn from the earlier O.R.D. data.<sup>5</sup> However, only through C.D. has the presence of the second of the two long-wave length maxima (negative for the (*R*)-configuration) been detected: as in the case of the related bridged 2,2'-dimethylbiphenyls discussed in part I,<sup>1</sup> the O.R.D. tailings of the conjugation band Cotton effect had in effect swallowed the small Cotton effect associated with this transition.

The conjugation band Cotton effect in the biphenyls has been demonstrated by C.D.<sup>1</sup> as well as by O.R.D.<sup>5</sup> measurements. Although we were not able to extend measurements below 260 m $\mu$  in the case of XXI-XXII, the conjugation band Cotton effect is clearly displayed in the 2,2'-dichlorobiphenyls XXIII-XXIV (Fig. 10) in the form of two adjacent high-intensity C.D. maxima

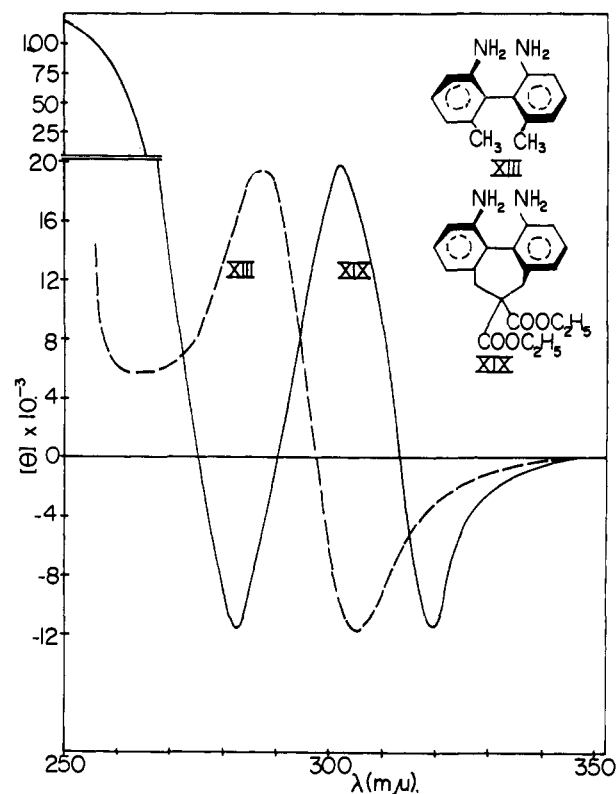


Fig. 15.

centered at 240 m $\mu$  which are positive for the (*R*)-configuration. This is precisely what might have been predicted on the basis of the O.R.D. behavior.<sup>5</sup>

**Conformation of Biphenyls and C.D.**—It has previously been established<sup>5</sup> that the high amplitude Cotton effect associated with the biphenyl conjugation band suffers a blue-shift as the bridge length is increased, in parallel with the blue-shift of the absorption

band itself which is known to accompany an increase in the angle of torsion around the pivotal 1,1'-bond. In the present work these conclusions have been confirmed in a study of (*R*)-9,10-dihydro-4,5-dimethylphenanthrene (XXV): in contrast to the seven-membered ring 2,2'-bridged biphenyls discussed in this and in the preceding paper,<sup>1</sup> the conjugation band Cotton effect has its C.D. maximum at 262 m $\mu$ , in excellent correspondence with the absorption maximum at 261 m $\mu$  (Fig. 11). In the previous O.R.D. study of this substance<sup>7</sup> only the long-wave length low-intensity features had been instrumentally accessible. Nevertheless, it had then been predicted that (*R*)-XXV would display a high-intensity positive Cotton effect centered near 261 m $\mu$ .<sup>7</sup> The present finding of  $[\theta]_{\max} +56,300$  (isooctane) at 262 m $\mu$  is in complete accord with this prediction, particularly when it is noted that the sample is not likely to be optically pure<sup>7</sup> and that the cited ellipticity therefore represents a *minimum* value.

Interpretation of the C.D. curves of the unbridged biphenyls offers, in general, difficulties similar to the ones encountered in the preceding O.R.D. study<sup>5</sup> of these compounds. For example, the diphenic acid derivatives IX–XII have relatively featureless C.D. curves in the instrumentally accessible region (Fig. 12). This is particularly unfortunate because a study of the O.R.D. or C.D. characteristics of unbridged compounds and a comparison of these characteristics with those of closely related bridged biphenyls of the same absolute configuration and (necessarily) fixed *cis*-conformation could, in principle, lead to important conformational conclusions, as in the case of the 2,2'-dinitrobiphenyls<sup>5</sup> and (below) the 2,2'-diaminobiphenyls. The subgroup of 6,6'-dihalo-2,2'-dimethylbiphenyls VI–VIII is of special interest. In the O.R.D. study it had been concluded<sup>5</sup> that a positive Cotton effect centered at 260–270 m $\mu$  corresponds to the (*R*)-configuration: the identical conclusion is now arrived at through comparison of the appropriate C.D. curves (Fig. 13). The problem of the conformation of amines will be discussed separately below.

**Summation of Chromophores.**—Inspection of the C.D. curve of the bridged dinitroketone XV (Fig. 14) shows that there is a marked deviation from the pattern set by the other bridged 2,2'-dinitrobiphenyls (Fig. 3 and 4). This deviation had also been noted in the preceding O.R.D. study<sup>5</sup> and it had been remarked that the various chromophores appear to contribute individually to the resultant O.R.D. curve, as revealed by algebraic analysis. These conclusions have now been confirmed. The algebraic summation of the C.D. curves (in dioxane) of bridged (*S*)-2,2'-dinitrobiphenyl XVI and of (*S*)-dimethyldibenzuberone (a bridged biphenyl ketone) bears a fair resemblance to the experimental curve for (*S*)-XV (Fig. 14).

**Comparison of C.D. and O.R.D. Results.**—The phenomena of C.D. and O.R.D. are complementary manifestations of the Cotton effect which is associated with a particular electronic transition.<sup>1</sup> The recent introduction of automatic recording instrumentation suitable for measuring C.D. curves has permitted a close examination of the relative merits of the two types of measurement in stereochemical studies. In connection with another problem, a preliminary judgment of the relative advantages of C.D. and O.R.D. had been arrived at.<sup>8</sup> The present investigation has yielded further information on this point.

*In certain ways the C.D. information has merely been of a confirmatory nature.* First, all of the conclusions which had previously been drawn, on the basis of O.R.D. information alone, concerning the relation between absolute configuration of various chromophores and sign of the relevant Cotton effects, have been confirmed *without exception* by the present and by the preceding<sup>1</sup> C.D. studies. Second, the presence, sign and intensity of the various Cotton effects discussed in the O.R.D. study<sup>5</sup> have been verified in this and the preceding<sup>1</sup> investigation by the observation of C.D. curves (a) which are centered near the point of inflection of the corresponding O.R.D. curves, (b) whose sign is the same as that of the corresponding O.R.D. curves, and (c) whose intensity (expressed in terms of ellipticity) reflects qualitatively the amplitude of the corresponding O.R.D. curves.

*On occasion, C.D. measurements have been of distinct advantage over O.R.D. measurements.* Thus, while all major Cotton effects had been detected by O.R.D.,<sup>5</sup> the presence of some low-intensity Cotton effects had previously escaped scrutiny. The corresponding low-amplitude O.R.D. curves had either been entirely hidden by the overlapping tails of Cotton effects, associated with nearby electronic transitions, or their presence had merely been suggested by barely discernible inflections in the over-all O.R.D. spectrum. Examples of the first kind were amply provided by the present study and have been discussed above. An example of the second kind is given by unbridged and bridged amines XIII and XIX, for which O.R.D. data<sup>5</sup> had been of very limited value because of the obvious extreme overlapping of curves. The then stated reservations<sup>5</sup> have now been resolved by the anticipated<sup>5</sup> identification of the optically active transitions. As shown in Fig. 15, the amines of the same absolute (*R*)-configuration show similar long-wave length features of the same sign: the red-shift of the curve for XIX corresponds to the red-shift of the aniline band maximum from 286 m $\mu$  (XIII) to 302 m $\mu$  (XIX).<sup>5</sup> By contrast, the C.D. curves of the acid solutions XIV and XX are of such low intensity (to ca. 300 m $\mu$  under the same conditions of measurement) that they are indistinguishable from zero on the same plot. It had been pointed out before that protonation quenches the aniline band in the absorption spectrum.<sup>5</sup> It can therefore be unequivocally stated that the long-wave length aniline band is optically active and that it is of the same sign for the bridged and unbridged amines of the same absolute configuration. Furthermore, it is not unreasonable to suggest that the unbridged amine XIII is *conformationally* related to the bridged amine XIX which has both the same absolute configuration and the identically signed C.D. pattern. Since the bridged amine is necessarily *cis* (or *syn*), it may be concluded that the unbridged amine is also *cis*. This result is of considerable interest since it had earlier been proposed<sup>9</sup> that amine XIII may be *trans* (or *anti*) and that protonation, which inverts the sign of rotation in the visible region, may cause a change in quadrant from *trans* to *cis*.<sup>10</sup> That the situation might be more complex had already been suggested<sup>5</sup> by the preliminary O.R.D. data.

To this example of the usefulness of C.D. in the conformational analysis of complex chromophores should be added the further advantage, noted repeatedly in the present work, that C.D. measurements may reveal

(9) D. D. Fitts, M. Siegel and K. Mislow, *ibid.*, **80**, 480 (1958); cf. also H. Musso and J. Sandrock, *Angew. Chem.*, **72**, 322 (1960).

(10) E. Bergmann and L. Engel, *Z. physik. Chem.*, **153B**, 85 (1931), had previously assigned the *cis* conformation to XIII on the basis of dipole moment measurements.

(7) K. Mislow and H. B. Hopps, *J. Am. Chem. Soc.*, **84**, 3018 (1962).

(8) C. Djerassi, H. Wolf and E. Bunnenberg, *ibid.*, **84**, 4552 (1962).

transitions—necessarily optically active—which are hidden even in the absorption spectrum itself.

On other occasions, O.R.D. measurements have afforded valuable information which could not have readily been culled from present C.D. data. The very tailing of the O.R.D. curves which has been cited as a disadvantage in the preceding discussion can be turned to excellent advantage<sup>7,8</sup>: the presence of high-intensity Cotton effects lying in wave length regions which are at present spectropolarimetrically and spectrodichrometrically inaccessible (“invisible giants”) can often be easily and unequivocally inferred by an examination of the long-wave length O.R.D. region. For example, it had previously been noted<sup>6,7</sup> that background rotations from a curve centered at short wave lengths is superimposed on all but one of the O.R.D. curves of simple six- and seven-membered ring bridged 1,1'-binaphthyls and 2,2'-dimethyl- and 2,2'-dichlorobiphenyls.<sup>11</sup> This curve dominates the whole visible region and is opposite in sign to that of the interposed conjugation band Cotton effect at 240–245 m $\mu$  and the binaphthyl band Cotton effects in the 250–330 m $\mu$  region. The position (i.e., below 220 m $\mu$  for the biphenyls and below 240 m $\mu$  for the binaphthyls) and the sign of this high-amplitude Cotton effect had been clearly discerned in the O.R.D. study. In fact, so dominant is the background rotation in the visible due to this Cotton effect that a fairly

(11) It is not unlikely that the background rotation in the case of the one exception (compound XXI in the present study) also makes a weak contribution to the O.R.D. in the visible region, but it has not thus far been possible to demonstrate such an effect experimentally.<sup>5</sup>

successful correlation of sign of rotation at the sodium D-line and absolute configuration in the biphenyl series (the Bridge rule) had at one time been established.<sup>9,11</sup> By contrast, in the C.D. study only compound XXXV clearly displays a short-wave length maximum, while compounds XXIV and XXV show bare intimations of this effect.

A judicious use of both C.D. and O.R.D. information is therefore clearly indicated. Present instrumentation dictates that “invisible giants” are best detected by O.R.D. measurements since their Cotton effects are felt as background curves and frequently even as the dominant effect of optical rotatory power in the region under investigation. On the other hand, C.D. is most useful in identifying relatively weak optically active transitions, especially in the longer wave length region where their presence may be obscured in both absorption and O.R.D. spectra by broad, overlapping neighboring bands.

### Experimental

Circular dichroism measurements were conducted in the solvents presented in Table I using a Baird-Atomic/Jouan Dichrograph (model JO-1). The concentrations employed (Table I) were such as to maintain the slit width below 1.3 mm. in the region of the circular dichroism maximum. The molecular ellipticity  $[\theta]$  is expressed<sup>1</sup> as  $[\theta] = 2.303(4500/\pi)(\epsilon_L - \epsilon_R)$  with  $(\epsilon_L - \epsilon_R) = d \times \text{sensitivity} \times 10^{-4} \times \text{mol. wt.}/c \times l$ , where  $d$  is the recorder deflection (in mm.) at the particular sensitivity setting (1.5, 2 or 3) of the instrument,  $c$  is the concentration in g./l. and  $l$  is the cell path length in cm.

Pertinent absorption spectra were obtained using an Applied Physics Corporation model 14 spectrophotometer.

---

## COMMUNICATIONS TO THE EDITOR

---

### THE METAL-METAL BONDED, POLYNUCLEAR COMPLEX ANION IN CsReCl<sub>4</sub>

Sir:

We present here a brief preliminary report of a recently determined structure which we believe provides a key to understanding various aspects of the chemistry of rhenium in its +3 oxidation state and probably has important implications regarding the chemistry of some other heavy transition elements.

Despite its rather innocent looking formula, CsReCl<sub>4</sub> was found to have a large orthorhombic unit cell ( $a = 14.06 \text{ \AA}$ ,  $b = 14.00 \text{ \AA}$ ,  $c = 10.69 \text{ \AA}$ ) containing twelve of the above formula units. The possibility of an unexpectedly complicated structure thus was suggested at a very early stage. From systematic absences, the possible space group could be limited to Cmc<sub>2</sub>, Cmc<sub>2</sub><sup>1</sup> and Ama<sub>2</sub>. By conventional statistical treatment<sup>1</sup> of the distribution of intensities in the principal zones, the last space group (a non-centric one) was unambiguously indicated. A positive piezoelectric test and the complete success of the ultimate refinement of the structure leave no doubt that this choice is correct.

Using some 580 reflections, a three-dimensional Patterson synthesis was computed and rhenium and cesium positions were eventually established by semi-systematic use of minimum functions of several ranks.<sup>2</sup> Using only these heavy atoms for phasing, a structure factor calculation was made giving a discrepancy index,  $R$ , of only 35%, thus indicating the probable correct-

ness of the heavy atom coordinates. One cycle of least squares refinements then was run varying all parameters and a Geller correlation matrix constructed. This showed several strong parameter interactions and refinement thus was continued allowing only those parameters which did not interact strongly to vary simultaneously. Ten such cycles reduced  $R$  (for Re and Cs only) to 18%. A difference Fourier map, in which the heavy atoms were subtracted out, revealed the chlorine positions quite clearly. After a number of cycles of full-matrix, least squares refinement, the discrepancy index had dropped to 7.3%, and a difference Fourier synthesis showed no anomalies.

The structure of the complex anion is shown in perspective in Fig. 1. Some of the important bond lengths (in Angstroms) and bond angles (in degrees), with estimated standard deviations in parentheses, are

$$\begin{aligned} \text{Re}_I\text{-Re}_{II} &= \text{Re}_{II}\text{-Re}'_{II} = 2.47 (0.01) \\ \text{Re-Cl (bridging)} &= 2.39 (0.03) \\ \text{Re-Cl (out of plane)} &= 2.36 (0.03) \\ \text{Re-Cl (in plane)} &= 2.52 (0.03) \\ \text{Cl}_7\text{-Cl}_5 &= \text{Cl}_7\text{-Cl}_3 = \text{Cl}_7\text{-Cl}'_7 = \text{Cl}_5\text{-Cl}_3, \text{ etc.} = 3.28 (0.06) \\ \langle \text{Cl}_5\text{Re}_{II}\text{Cl}_4 \rangle &= \langle \text{Cl}_5\text{Re}'_{II}\text{Cl}'_4 \rangle, \text{ etc.} = 91^\circ (1.0) \\ \langle \text{Cl}_5\text{Re}_I\text{Cl}_3 \rangle &= \langle \text{Cl}_5\text{Re}_I\text{Cl}_3 \rangle, \text{ etc.} = 79^\circ (1.0) \end{aligned}$$

While the  $[\text{Re}_3\text{Cl}_{12}]^{3-}$  ion is required crystallographically to have only one plane of symmetry (passing through  $\text{Re}_I$  and bisecting the  $\text{Re}_{II}\text{-Re}'_{II}$  line) it actually exhibits  $D_{3h}$  symmetry within experimental uncertainties. Hence, only the mean values of the various types of Re-Cl distances are quoted above.

The five chlorine atoms bound to each rhenium atom lie approximately at five of the apices of an octahe-

(1) E. R. Howells, D. C. Phillips and D. Rogers, *Acta Cryst.*, **3**, 210 (1950).

(2) M. J. Buerger, "Vector Space," John Wiley and Sons, Inc., New York, N. Y., 1961.