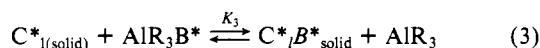
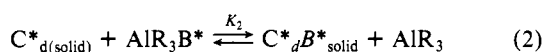
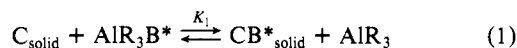


to that of the recovered monomer, the enantiomeric excess decreasing by increasing conversion (experiments 6-9).

The above experiments clearly show the existence, in the catalytic system used, of at least two classes of catalytic centers. The first one is made of highly stereospecific, catalytic centers (C_1 and C_d)⁸ which are stereoelective and prevailing polymerize the (*R*)-antipode of the monomer producing the highly isotactic diisopropyl ether insoluble polymer. The second class that synthesizes the amorphous ethyl acetate soluble polymer (*C*), is made of substantially nonstereospecific catalytic centers that have a very low stereoelectivity, if any. For this last type of centers not only the productivity but also the relative activity and/or concentration in the catalyst decreases by increasing *r*.

The stereoregulating and antipode discriminating capacity of the optically active Lewis base can satisfactorily be explained by assuming the following: (i) (-)-MA, as Lewis base (B^*), substantially decreases the number and/or the activity of the nonstereospecific catalytic centers, *C*, which evidently possess a Lewis acidity larger than AlR_3 (eq 1); (ii) stereoelective, highly



stereospecific, chiral centers (C^*_d ; C^*_l) are, probably for steric reasons, weaker Lewis acids than the less stereospecific centers *C* [$K_1 > K_2$ and $K_1 > K_3$ (eq 1-3)]; (iii) the observed stereoelectivity in the synthesis of the most stereoregular fraction is due to the different tendencies of the chiral catalytic centers (C^*_d ; C^*_l) to form complexes (and then to lose or decrease their catalytic activities) with the chiral base B^* , the equilibrium constants K_2 and K_3 being different, in keeping with the formation of the diastereomeric complexes $C^*_{dB^*}$ and $C^*_{lB^*}$, respectively.

We take the decrease of catalyst productivity by increasing *r* as an indication that the surface complexes CB^* , C_dB^* , and C_lB^* are not catalytically active. However, the present data do not exclude the existence of different stereoregulating and antipode discriminating mechanisms connected with the existence of other types of centers (C^*B^*) that might be still catalytically active and, because of the presence of the chiral base B^* , might be able to distinguish between the two antipodes of the monomer.⁹

Registry No. (\pm)-4-MH, 13643-03-3; (*l*)-MA, 4951-49-9; isotactic poly(\pm)-4-methyl-1-hexene, 33409-74-4; poly(\pm)-4-methyl-1-hexene, 30775-40-7; $TiCl_4$, 7550-45-0; $MgCl_2$, 7786-30-3; $Al(i-C_4H_9)_3$, 100-99-2.

(9) Pino, P.; Mülhaupt, R., to be submitted for publication.

Circular Dichroism Spectrum of C_3 -Cyclotriguaiacylene after Ionization of the Phenolic Groups. Experimental Approach to the "Magic Angle" Region in C_3 -Cyclotrimeratrylene Derivatives

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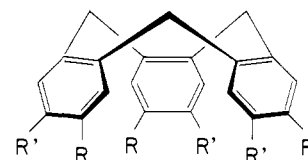
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In previous papers,^{1,4} we reported the circular dichroism (CD) spectra of some C_3 -chiral derivatives of cyclotrimeratrylene (CTV) and their interpretation in terms of exciton coupling between the

transition moments of the three aryl chromophores. The presence of substituents having spectroscopic moments of different magnitudes ($R \neq R'$) was considered to cause a rotation of the electric transition moments of each individual aryl chromophore from the symmetrical positions ($\theta = 0$ or 90°); in this way, collinear components of the magnetic and electric moments are generated in the "trimer" (Figure 1). In the exciton approximation, the symmetric *A* coupling depicted in Figure 1 generates a high-energy negative CD component for the B_{2u} transition and a low-energy positive component for the B_{1u} . In the CD spectrum of (*M*)-(+)- C_3 -cyclotriguaiacylene **1** in methanol (Figure 2), these



M-(+) **1** $R = OCH_3$
 $R' = OH$

components correspond to the bands observed at ca. 277 and 250 nm; the bands at ca. 299 and 236 nm correspond instead to the degenerate *E* components of the two transitions.¹

This picture is true as long as the value of θ is less than $\sim 45^\circ$, which represents in the point-dipole approximation the "magic angle" θ_m at which the potential *V* is zero.¹¹

$$V = (D_{\text{mon}}/d^3)(\cos^2 \theta \cos^2 \Phi + \frac{1}{4} \cos^2 \theta \sin^2 \Phi - \frac{1}{4} \sin^2 \theta) \quad (1)$$

When $45^\circ < \theta < 90^\circ$, the symmetric *A* coupling of the B_{2u} transitions still corresponds to a negative CD, but this time at lower energy; similarly, for $180^\circ - 45^\circ < \theta + 90^\circ < 180^\circ$, the *A* coupling of the B_{1u} transitions always gives positive CD, but now at higher energy; in other words, the sequence of bands should be inverted with the overall effect of generating a mirror image spectrum.¹³

The value of θ in all C_3 -CTV derivatives studied so far is usually small, and in order to reach the region of the "magic angle", substituents *R* and R' should have spectroscopic moments of very different magnitude. We expected that such a situation could be obtained in (*M*)-(+)-**1**, after ionization of the phenolic groups. As our previous work has shown,¹ when the phenolic groups are undissociated (in neutral or acidic methanol), their spectroscopic moment is slightly higher than the methoxy one, and the value of θ was calculated to be of the order of $3-4^\circ$. Ionization of **1** (in 0.2 N sodium methoxide/methanol solution) determines, as expected,³ a ca. 2-fold increase of the band areas of both the B_{2u} and B_{1u} transitions in the isotropic absorption spectrum, and a shift to longer wavelengths of all observed bands (Figure 2). Guaiacol, which represents the "active monomer" of trimer **1**, shows a ca. 3-fold increase in the band area of the B_{2u} transition on passing from acid methanol to a 0.2 N solution of sodium methoxide in methanol. The band areas of both B_{2u} and B_{1u} transitions of **1** are about 40% larger than 3 times the values observed for guaiacol, indicating nonadditive contributions to the total isotropic intensity which are probably due to homoconjugation effects. After subtraction of these contributions, the increase in the absorption band areas of **1** after ionization becomes comparable to that of guaiacol.

In the case of strongly conjugative substituents such as OCH_3 and particularly O^- ,⁵ it is not possible to predict quantitatively

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(5) Murrell, J. N. "The Theory of the Electronic Spectra of Organic Molecules"; Methuen: London, 1963, p 21.

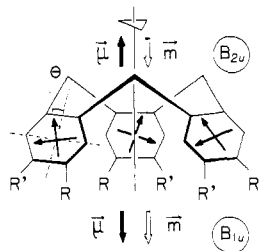


Figure 1. In-phase (A) coupling of the B_{2u} and B_{1u} electric transition moments. For $\theta < 45^\circ$ the interaction potential is repulsive for the B_{2u} and attractive for the B_{1u} transition.

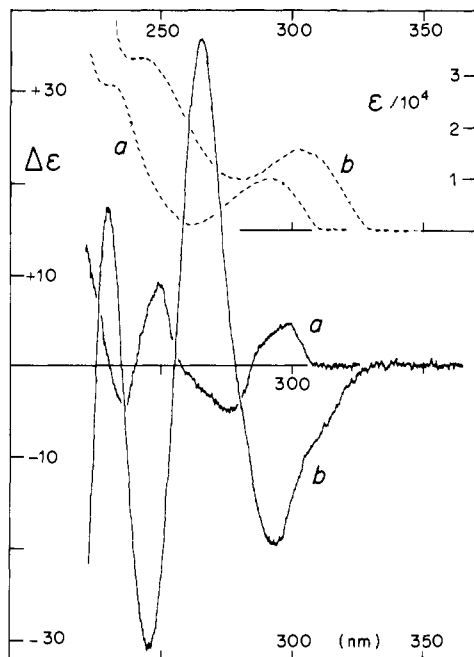


Figure 2. Circular dichroism spectra (—) and isotropic absorption spectra (---) of (*M*)-(+)-1: (a) in methanol; (b) in 0.2 N sodium methoxide in methanol.^{9,10}

the total absorption intensity from addition laws: both "quadratic"⁶ and "linear"⁷ approaches usually give calculated values higher than those observed.⁸ As our problem is to calculate the variation of θ corresponding to a 3-fold increment of the absorption intensity, due to the variation of the spectroscopic moment of a single substituent, the computed value might therefore be too small. Nevertheless, by use of the "linear law", which gives correct values for *o*-dimethoxybenzene,⁷ a variation of θ around 40° was obtained. Since the value of θ before ionization was $3\text{--}4^\circ$, the expected overall rotation of the electric moments should effectively fall in the region of the "magic angle".

The experimental CD spectrum of (*M*)-(+)-1 in 0.2 N sodium methoxide/methanol solution (Figure 2) shows a dramatic change with respect to that of the un-ionized triphenol, consisting of an apparent inversion of all CD bands and a 5-fold increase in the intensities. However, considering the shift to longer wavelengths of the UV λ_{max} in the ionized vs. the un-ionized species, the pair of oppositely signed bands at 246 nm ($\Delta\epsilon = -30$) and 265 nm ($\Delta\epsilon = +34$) should most probably be assigned to the exciton splitting of the B_{1u} transition (rather than the pair 230–246 nm), and the band at 293 nm ($\Delta\epsilon = -18$) would then represent the high-energy negative component of the B_{2u} couplet. Thus, if these attributions

Table I. Rotational Strengths of the B_{1u} Transition of Ionized 1 as a Function of Angle θ ^{a,b}

θ , deg	$\Delta\bar{\nu}$, cm^{-1}	$10^{40}R_{\text{cor}}$, cgsu	θ , deg	$\Delta\bar{\nu}$, cm^{-1}	$10^{40}R_{\text{cor}}$, cgsu
0	1632	0	36	460	37
10	1530	44	38	346	28
20	1235	66	40	230	18
30	783	57	42	112	10
34	571	44	44	0	0

^a Calculated with $D_{\text{mon}} = 8.8 \times 10^{-36}$ cgsu, by using $(\theta + 90^\circ)$ instead of θ in eq 1. ^b See ref 13.

are correct, there is no inversion of the CD bands upon ionization and the value of θ should therefore be smaller than 45° . An additional CD shoulder at 305 nm could possibly explain the absence of the positive component of the B_{2u} couplet at ca. 310 nm. The origin of this contribution is not easily explainable, however.

In view of the nearly perfect shape of the B_{1u} couplet (observed rotational strengths⁹ -20×10^{-40} and $+21 \times 10^{-40}$ cgsu, from high to low energy), it seemed feasible to estimate angle θ through a semiquantitative calculation of the CD intensity. The dipole strength D_{mon} of the B_{1u} transition was estimated from the UV spectrum of ionized guaiacol to be in the range of $(8.8 \pm 1.7) \times 10^{-36}$ cgsu. The theoretical rotational strength, R , given by expression 2¹¹ was corrected for cancellation effects by using the

$$R = 3\pi\bar{\nu}rD_{\text{mon}} \cos \theta \sin \theta \cos \Phi \quad (2)$$

relation¹² $R_{\text{cor}} = R\Delta\bar{\nu}/\sigma$, in which σ is the half-band width of the B_{1u} UV band in ionized guaiacol (ca. 4200 cm^{-1}), and $\Delta\bar{\nu}$ is the theoretical splitting of the exciton couplet, obtained from expression 1 by the relation $\Delta\bar{\nu} = 3V/hc$. The values of $\Delta\bar{\nu}$ and R_{cor} are assembled in Table I as a function of θ . These data suggest a value of θ in the range $36\text{--}42^\circ$ for ionized 1, in good agreement with that deduced above from the "linear law" of Ballester.⁷

Summarizing, the changes observed in the CD spectrum of C_3 -cyclotriguaiacylene after ionization of the phenolic groups seem to be reasonably well explained in the light of the exciton theory, by using the concept of spectroscopic moments. In 1, the rotation of the electric transition moments upon ionization probably reaches, but does not cross, the region of the "magic angle". This observed behavior suggests the study of related C_3 -triphenols in which the OCH_3 groups would be replaced by substituents having slightly smaller spectroscopic moments such as more bulky *O*-alkyl groups,^{2,4} in order to explore more closely the critical region of θ .

Acknowledgment. We are grateful to one of the referees for constructive criticisms; G. G. thanks CNR (Rome) for financial support.

(9) The sample of (*M*)-(+)-1 studied was considered to be $>90\%$ enantiomerically pure; it exhibited $[\alpha]_{\text{D}}^{25} +253^\circ$ in chloroform (c 0.13), $[\alpha]_{\text{D}}^{25} +163^\circ$ in neutral methanol (c 0.03), and $[\alpha]_{\text{D}}^{25} -117^\circ$ in 0.2 N sodium methoxide in methanol (c 0.03).

(10) The CD spectra were recorded on a Jouan-Dichrograph II instrument, and the UV spectra on a Perkin-Elmer 554 spectrometer.

(11) The geometry of the CTV system can be defined^{2b} by r (2.78 Å), the distance between the center of each phenyl ring and the C_3 axis, d (4.79 Å), the distance between the centers of two phenyl rings, and by Φ ($43 \pm 2^\circ$), the angle of the plane of a phenyl ring with the C_3 axis. With these data, the "magic angle" (θ_m) is found to be $46 \pm 0.4^\circ$.

(12) For a discussion of overlapping and cancellation effects, see: Mason, S. F.; Seal, R. H.; Roberts, D. R. *Tetrahedron* 1974, 30, 1671.

(13) **Note Added in Proof:** Strictly speaking, the magic angle is reached for the B_{2u} transition when $\theta = \theta_m = 46^\circ$ and for the B_{1u} transition when $(\theta + 90^\circ) = (180^\circ - \theta_m)$, i.e., when $\theta = 44^\circ$. Accordingly, the vanishing of B_{2u} and B_{1u} transitions in the CD spectra should not occur *simultaneously*. However, the difference is clearly too small to be experimentally observable; this is why we have adopted a mean value of $\theta_m \sim 45^\circ$ defining a *magic angle region*, rather than a precise value, which would be irrelevant in view of the approximation employed in the calculation of V .

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