

# Stereochemistry of Allenic Compounds. 3. Geometrical Deformations of the Propadiene Unit in Cyclic Allenes<sup>1</sup>

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**Abstract:** The structures of phenylurethane derivatives of cyclic allenes **7** were investigated by X-ray analysis. **7a** and **7c** form analogous pairs of homochiral chains and spontaneous resolution has been observed for **7b** and **7c**. Bending and twisting of the cumulated system were evidenced. Deviations from the ideal geometry, which were predicted by theoretical calculations, should be taken into account in the interpretation of the chiroptical properties of allenic compounds.

Allenic compounds deserve a special interest from organic chemists, as the presence of two cumulated double bonds in a molecule frequently confers biological properties. It is worth mentioning various allenic steroids,<sup>3</sup> such as the allenic ketones **1**,<sup>4</sup> linear allenic acid derivatives **2**,<sup>5</sup> and allenic prostaglandins **3**<sup>6</sup> (Chart I).

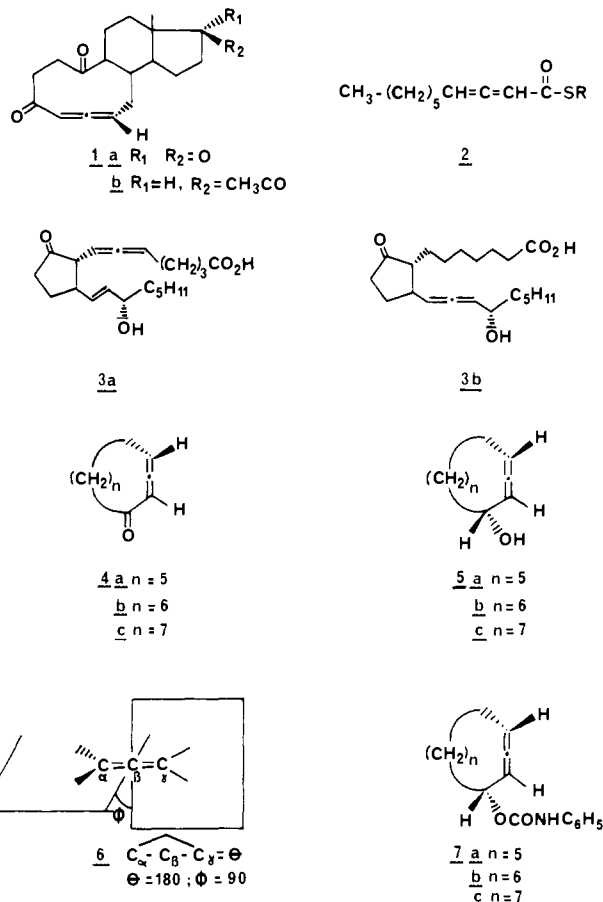
In this context, it is striking to note that stereochemical studies of allenes scarcely appear in the chemical literature.<sup>7</sup> Our initial program was the synthesis of optically active  $\alpha$ -cycloallenes **4** and -allenols **5**. As chiroptical methods seemed to us to be unsafe in establishing the configurations of these compounds, we turned to X-ray crystallography, which revealed unexpected features of the allene geometry.

Since van't Hoff prediction,<sup>8</sup> allenes have usually been represented as shown in formula **6**. Chiroptical methods, based on Lowe and Brewster's rule<sup>9</sup> and Mason's rule,<sup>10</sup> were used for the correlation of optical rotation and circular dichroism, respectively, assuming a  $D_{2d}$  symmetrical geometry of the allene unit. However, recent theoretical calculations<sup>11,12</sup> have predicted that, at least for some strained allenes (seven- and eight-membered rings), bending ( $\theta \neq 180^\circ$ ) and/or twisting ( $\phi \neq 90^\circ$ ) deformations are highly probable. Moreover, it has been calculated<sup>13,14</sup> that rotational strengths are associated with these deformations. The previous

Table I. Crystal Data

	7a	7b	7c
mol formula	C <sub>16</sub> H <sub>19</sub> NO <sub>2</sub>	C <sub>17</sub> H <sub>21</sub> NO <sub>2</sub>	C <sub>18</sub> H <sub>23</sub> NO <sub>2</sub>
mol wt	257.3	271.4	285.4
space group	<i>Pha</i> 2 <sub>1</sub>	<i>P4</i> <sub>1</sub>	<i>P2</i> <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
cell parameters, Å			
<i>a</i>	20.996 (5)	9.165 (5)	20.320 (7)
<i>b</i>	12.553 (3)	9.165 (5)	15.968 (7)
<i>c</i>	5.276 (2)	18.320 (10)	5.069 (5)
$\alpha = \beta = \gamma = 90^\circ$			
obsd data ( $I > 3\sigma(I)$ )	1063	1394	1400
reliability factor	0.067	0.057	0.066
molecules per cell	4	4	4
calcd density, g cm <sup>-3</sup>	1.23	1.17	1.15

Chart I



(1) Previous paper in this series: J. C. Damiano, J. L. Luche, and P. Crabbé, *Tetrahedron*, **34**, 3137 (1978). See also J. L. Luche, J. C. Damiano, P. Crabbé, C. Cohen-Addad, and J. Lajzerowicz, *ibid.*, **33**, 96 (1977).

(2) (a) Laboratoire de Chimie Organique; (b) Laboratoire de Spectrométrie Physique.

(3) Inter alia: (a) P. Crabbé, D. André, and H. Fillion, *Tetrahedron Lett.*, 893 (1979); (b) H. Westmijne and P. Vermeer, *ibid.*, 4101 (1979); (c) E. E. Galantay, R. V. Coombs, I. Bacso, R. L. Elton, and E. Harrington, *Experientia*, **28**, 771 (1972).

(4) H. L. Carrel, J. P. Glusker, D. F. Corey, F. H. Batzhold, and C. H. Robinson, *J. Am. Chem. Soc.*, **100**, 4282 (1978).

(5) M. Morisaki and K. Bloch, *Bioorg. Chem.*, **1**, 188 (1971).

(6) P. Baret, E. Barreiro, A. E. Greene, J. L. Luche, M. A. Teixeira, and P. Crabbé, *Tetrahedron*, **35**, 2931 (1979), and references cited therein.

(7) For recent papers see (a) A. Claesson and L. I. Olsson, *J. Am. Chem. Soc.*, **101**, 7302 (1979); (b) W. H. Pirkle and C. W. Boeder, *J. Org. Chem.*, **43**, 1950 (1978). For a review see R. Rossi and P. Diversi, *Synthesis*, 25 (1973).

(8) J. van't Hoff, "La Chimie dans l'Espace", P. M. Bazendijk, Rotterdam, 1875, p 29.

(9) G. Lowe, *Chem. Commun.*, 411 (1965); J. H. Brewster, *Top. Stereochem.*, **2**, 33 (1967). See also W. Runge and G. Kresze, *J. Am. Chem. Soc.*, **99**, 5597 (1977).

(10) P. Crabbé, E. Velarde, H. W. Anderson, S. D. Clarke, W. R. Drake, and S. F. Mason, *Chem. Commun.*, 1261 (1971). See also S. F. Mason and G. W. Vane, *Tetrahedron Lett.*, 1593 (1965); W. Runge and J. Winkler, *Ber. Bunsenges. Phys. Chem.*, **79**, 610 (1975); W. Runge, W. Kosbahn, and J. Winkler, *ibid.*, **79**, 381 (1975).

(11) P. W. Dillon and G. R. Underwood, *J. Am. Chem. Soc.*, **96**, 779 (1974).

(12) F. A. L. Anet and I. Yavari, *J. Am. Chem. Soc.*, **99**, 7640 (1977).

(13) A. Rauk, A. F. Drake, and S. F. Mason, *J. Am. Chem. Soc.*, **101**, 2284 (1979).

(14) H. Dickerson, S. Ferber, and F. S. Richardson, *Theor. Chim. Acta*, **42**, 333 (1976).

Table II. Comparative Data for the Geometry of the Allene Moiety

	7a	7b	7c
Angular Values			
$\phi^a$	-79.8 (5)	-80.0 (4)	-95.2 (6)
O(1)-C(1)-C(2)-C(3)	-171.9 (4)	-124.3 (3)	135.4 (5)
C(p)-C(1)-C(2)-C(3) <sup>b</sup>	72.2 (4)	117.5 (3)	12.0 (6)
O(2)-C(p+1)-C(1)-H(C1)	-28.9 (4)	15.0 (3)	35.8 (3)
O(1)-C(1)-C(2)-H(C2)	7.8 (6)	56.1 (3)	-42.6 (4)
H(C1)-C(1)-C(2)-C(3)	-50.3 (4)	-6.2 (3)	-109.9 (5)
H(C1)-C(1)-C(2)-H(C2)	129.5 (4)	174.2 (4)	72.1 (4)
$\theta^a$	168.0 (4)	170.7 (4)	179.3 (5)
Bond Lengths (Å)			
C(2)-C(3)	1.320 (7)	1.296 (4)	1.300 (5)
C(3)-C(4)	1.307 (7)	1.300 (5)	1.307 (5)

<sup>a</sup>  $\phi$  represents the dihedral angle between the principal planes of the allene, in this case C(1)C(2)C(3) and C(3)C(4)C(5).  $\theta$  represents the valence angle C(2)-C(3)-C(4). <sup>b</sup> Compound 7a,  $p = 9$ ; 7b,  $p = 10$ ; 7c,  $p = 11$ .

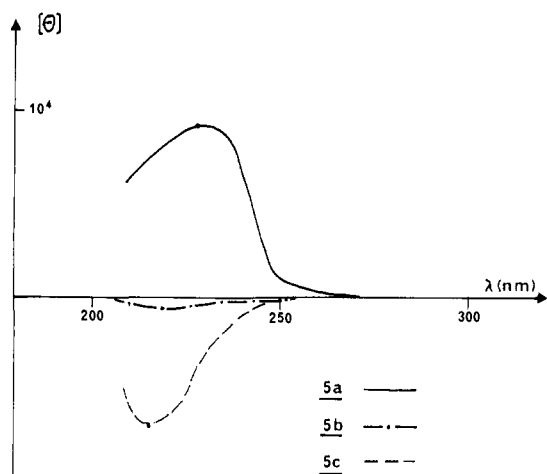


Figure 1. CD spectra of cycloallenois 5.

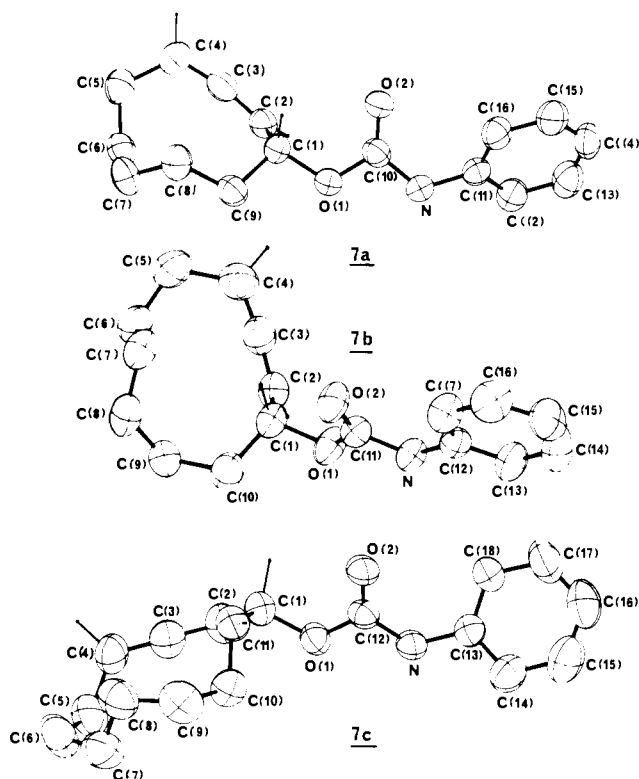


Figure 2. ORTEP projection of compounds 7 on C(3),C(4),C(5) plane; 50% probability ellipsoids are shown.

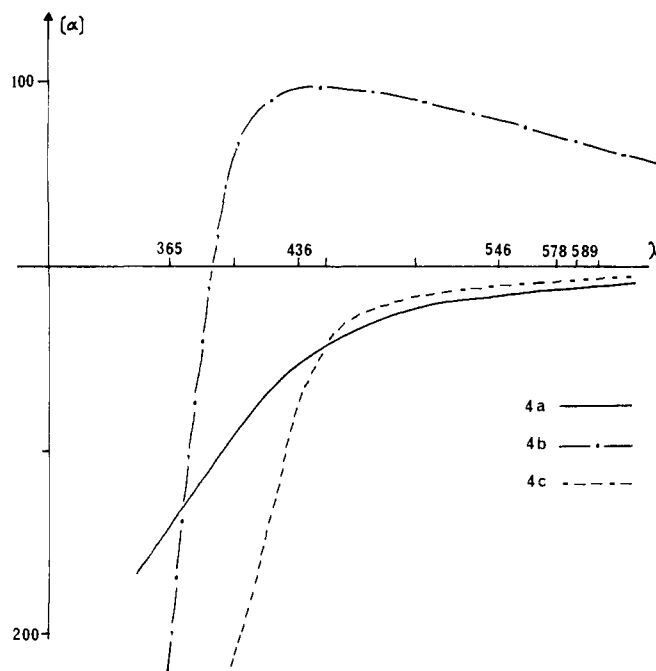


Figure 3. ORD spectra of cycloallenois 4.

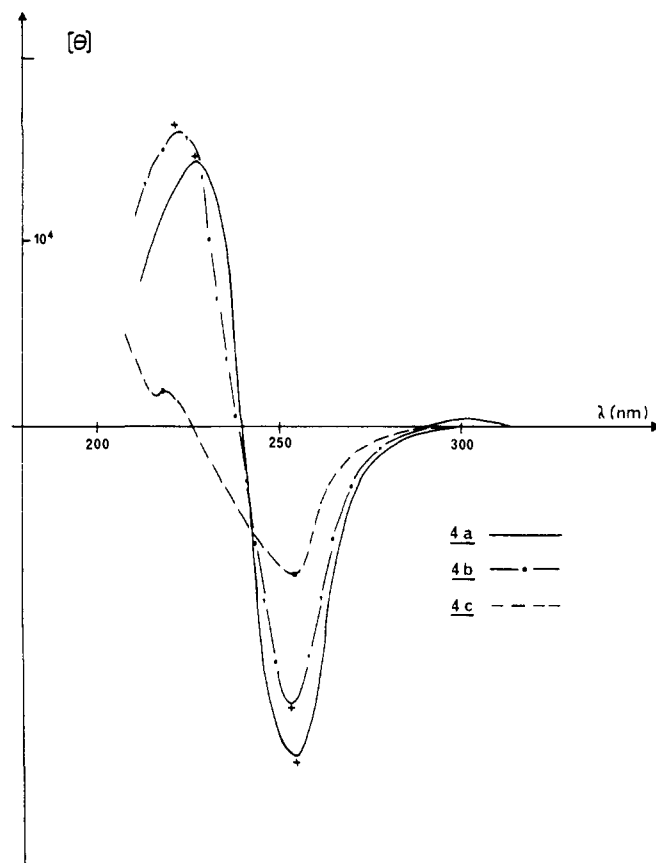


Figure 4. CD spectra of cycloallenois 4.

interpretations of the chiroptical properties of allenes, based on van't Hoff ideal geometry, therefore become questionable.

Allenic alcohols 5 were synthesized in the optically active form from (*R*)-(-)-cycloalken-2-ols.<sup>1,15</sup> Their absolute configuration, deduced from that of the parent compounds, has been unambiguously established as *RaR*(+).<sup>1</sup> Their CD spectra at 215–230 nm (lowest energy Cotton effect of the allene) were expected from

(15) J. L. Luche, J. C. Damiano, and P. Crabbè, *J. Chem. Res. (S)*, 32 (1977).

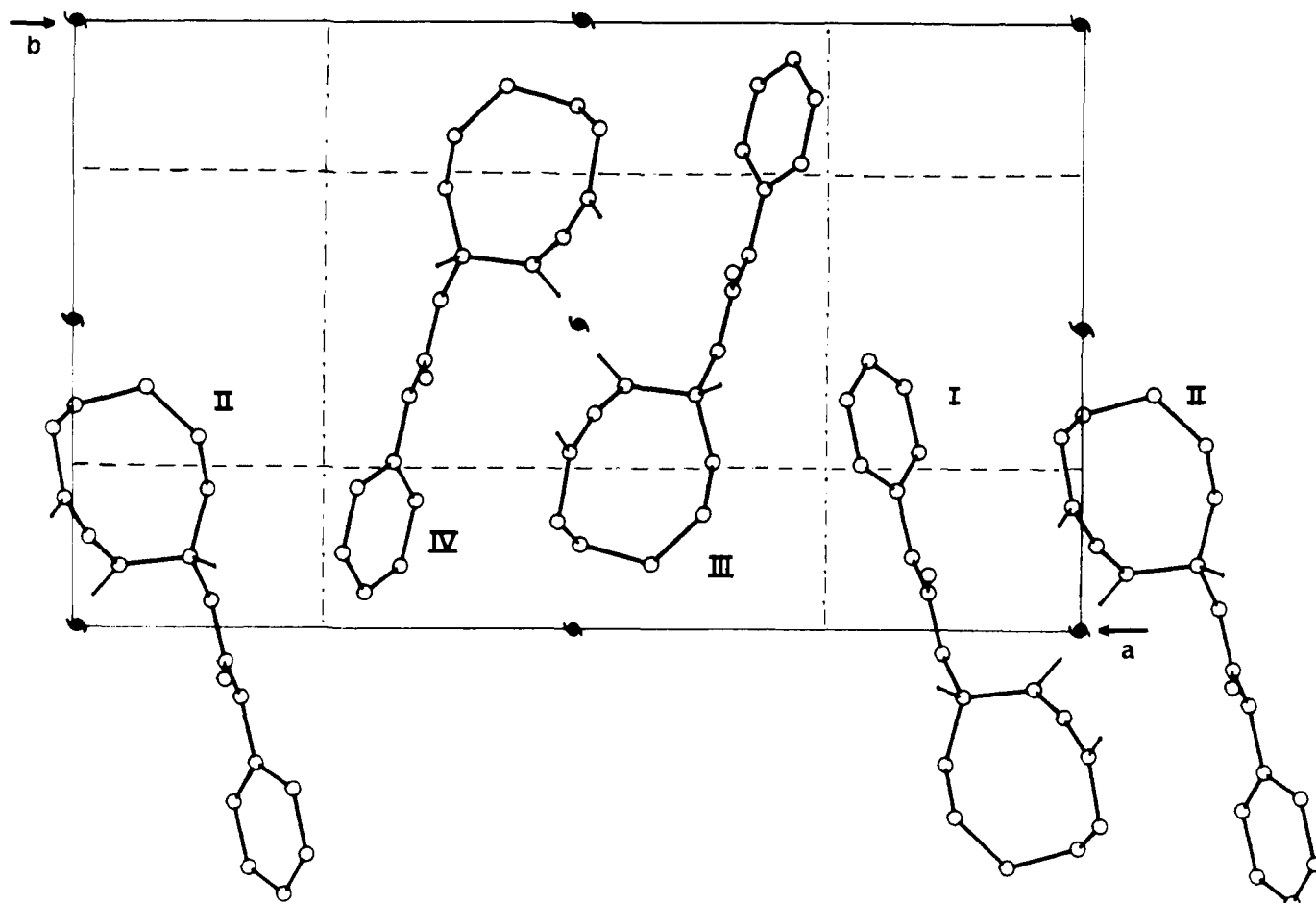


Figure 5. Compound **7a**: molecular packing along  $\bar{c}$ . I,  $(x, y, z)$ ; II,  $(1-x, -y, 1/2+z)$ ; III,  $(3/2-x, 1/2+y, 1/2+z)$ ; IV,  $(1/2+x, 1/2-y, z)$ .

the sector rule<sup>10</sup> to exhibit a positive peak. In fact, the observed values are (Figure 1) **5a**,  $\lambda_{\max}$  229 nm,  $[\theta]$  +9200; **5b**,  $\lambda_{\max}$  222 nm,  $[\theta]$  -585; **5c**,  $\lambda_{\max}$  215 nm,  $[\theta]$  -6930.

Such a variation for compounds which possess the same absolute configuration prompted us to investigate their precise geometries by X-ray analysis. Alcohols **5** were converted to their crystalline phenylurethanes **7**. The CD spectra of these compounds also revealed an unexpected variation: **7a**,  $\lambda_{\max}$  232 nm,  $[\theta]$  +7260; **7b**,  $\lambda_{\max}$  228 nm,  $[\theta]$  -25500; **7c**,  $\lambda_{\max}$  233 nm,  $[\theta]$  -2900.

Crystal structures were determined with the racemic mixtures **7a** and **7c** and optically active **7b**. Description of the method is given in the Experimental Section. Crystal data are summarized synoptically in Table I.

#### Allene Geometry

An analysis reveals interesting results at the molecular as well as intermolecular stage, as discussed below. A comparative scheme of the molecular structures is given in Figure 2 as ORTEP<sup>16</sup> drawings, in which the projection plane is the C(3)-C(4)-C(5) plane.

Significant angular values  $\theta$  and  $\phi$  given in Table II demonstrate, in the three cases investigated, the existence of deformations of the allene structure.

It is worth mentioning that the bending and twisting angles in **7b** are almost the same as those previously reported for **7a**,<sup>1</sup> although the ring strain is substantially decreased. More surprisingly, in compound **7c**  $\theta$  has the "normal" value (179.3°) but  $\phi$  reaches 95.2°. Such an "opening" of the dihedral angle indicates that the ring strain may not be the only factor which governs the geometry of the chromophore.

On the other hand, from inspection of the ORTEP drawings, the conformational analogy between **7a** and **7c** is evident. It is thus important to note that the analogy in the geometries of the allene

chromophore between **7a** and **7b** does not follow the ring conformation analogy between **7a** and **7c**. These discrepancies do not contribute to an understanding of the problem of the circular dichroism spectra, which depend strongly on the geometry of the chromophore and the conformation of the cycle.

The complexity of the chiroptical properties in the cycloallene series is further demonstrated by the variation of optical rotation of the cycloallenes **4**. Oxidation of alcohols **5** yields ketones **4** for which the *R* absolute configuration has been firmly established.<sup>1</sup> Their optical rotation at 589 nm is negative for **4a** and **4c** but positive for **4b**. This result underscores the fact that Lowe-Brewster's rule, which predicts in the three cases **4a-c** a negative  $[\alpha]_D$ , can be misleading even in a *homologous* series.

The optical rotation, as shown in Figure 3, varies unexpectedly and has not been satisfactorily interpreted.

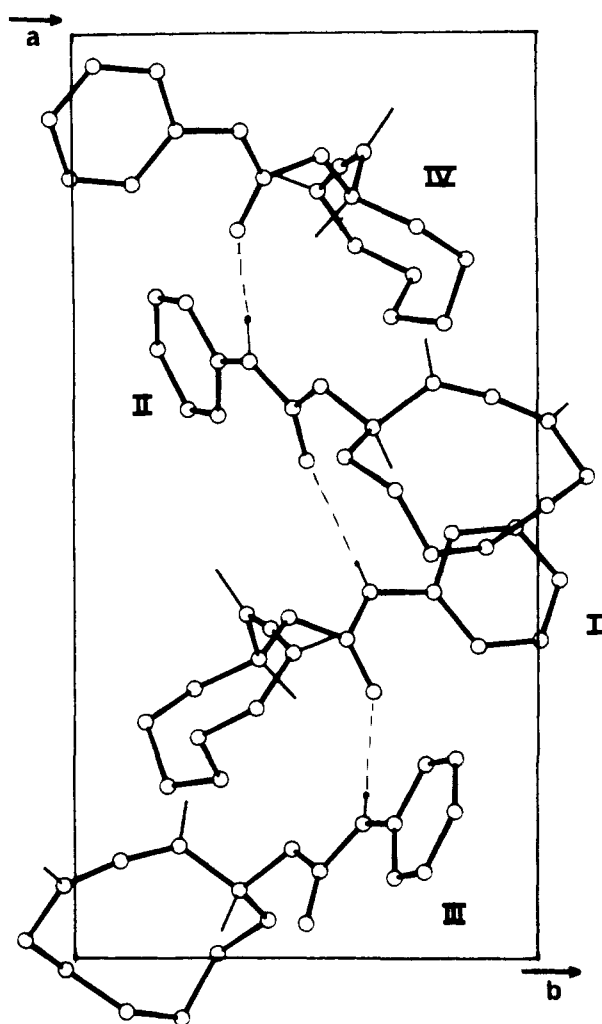
The CD curves of ketones **4** (Figure 4) display two Cotton effects, one negative at 254 nm, the second positive at ca. 215-230 nm. By contrast with the cases of compounds **5** and **7**, there is no change in the signs with the size of the ring. Ketone **1a** displays four Cotton effects, a weak negative one at 327 nm ( $[\theta]$  -480) and three positive ones at 293 ( $[\theta]$  +16000), 541 ( $[\theta]$  +30000), and 215 nm ( $[\theta]$  +20000), but the presence of a second C=O group in the ring should contribute to the complexity of the spectrum.<sup>17</sup>

Thus, the relationship of structure to chiroptical properties appears to be unreliable for allenic compounds. This situation is due, in part, to the very small number of allenes for which the exact geometry is known.<sup>18</sup> It is therefore not presently possible

(17) Compound **1a** was kindly supplied by Professor C. H. Robinson, whom we wish to thank.  $[\theta]$  values are given in order of magnitude. For X-ray analysis of compound **1**, see ref 4.

(18) From the Cambridge crystallographic Data Centre, we obtained allenic structures on which X-ray analysis has been carried out. We have not considered organometallic complexes, owing to their particularities. Among the remaining eight structures (most of which are achiral), the chiroptical properties in the chiral compounds have not been published.

(16) C. K. Johnson, ORTEP, Report ORNL 3794, Oak Ridge National Laboratory, Oak Ridge, Tenn. 1965.



**Figure 6.** Compound **7b**: molecular packing along  $\bar{a}$ . I,  $(x, y, z)$ ; II,  $(1 - y, x, 1/4 + z)$ ; III,  $(y, 1 - x, z - 1/4)$ ; IV,  $(1 - x, 1 - y, 1/2 + z)$ .

to determine in which cases deformation of the allenic linkage exists, and its precise influence on the CD spectra and optical rotatory power. In other words, the problem is to choose between an achiral first sphere (inherently symmetric asymmetrically perturbed)<sup>19</sup> or a chiral first sphere (inherently dissymmetric) for the allenic chromophore. We have demonstrated experimentally that the first (classical) situation does not reflect reality in every case. However, the small number of examples does not permit a conclusion to be drawn as to the generality of the second representation.

### Intermolecular Relationships

As indicated above, crystal structures were determined with **7a** and **7c** in the racemic form. This choice permitted a study of the intermolecular linkages which provided some interesting results. Compound **7a** crystallizes as a racemate, and **7c** as a conglomerate. The molecular packing is shown in Figures 5 and 7.

In compounds **7a** and **7c**, the molecules related by the  $\bar{c}$  axis translation are linked by an intermolecular hydrogen bond. They form pairs of homochiral chains around a twofold screw axis. In **7a**, one molecular chain pair is related to the other by a mirror plane  $n$ , while in **7c** they correspond by a twofold screw axis.

From the structural analogy between **7a** and **7c**, it was expected that optically active **7a** should be isomorphous to **7c**. This assumption was confirmed by oscillation and Weissenberg photographs which gave for the (+) enantiomer of **7a** space group  $P2_12_12_1$ ,  $a = 21.2$  (2),  $b = 12.80$  (5),  $c = 5.30$  (5) Å,  $z = 4$ .

(19) G. Sznatzke, *Angew. Chem., Int. Ed. Engl.*, **18**, 363 (1979).

Spontaneous resolution observed in the series can be compared with different examples in other series.<sup>20</sup> It is worth noting in this particular case that a difference of two methylene units in the ring size is sufficient to induce the crystallization of a racemic mixture in two different modes, while the corresponding enantiomers are isomorphous.

A spontaneous resolution was also observed with **7b**, for which optically active crystals were obtained from a racemic solution in petroleum ether. Surprisingly in this compound a difference of only one methylene unit with respect to **7a** or **7c** results in important differences in the molecular arrangement ( $P4_1$  group; see Figure 6), the ring conformation, and the chiroptical properties.

### Experimental Section

IR spectra were recorded on a Beckman Acculab 4 instrument in film or in  $CCl_4$  solution. UV spectra were taken in EtOH solution on a Beckman DBT spectrometer. NMR spectra were recorded at room temperature on a 60-MHz JEOL PMX60 spectrometer, with  $CDCl_3$  containing  $Me_4Si$  as an internal standard, except for trimethylsilyl derivatives, where  $CHCl_3$  was used ( $\delta_{CHCl_3}$ , 7.24 ppm). Resonance frequencies are quoted in parts per million downfield from  $Me_4Si$  and are accurate to 0.01 ppm. Melting points were determined with a Büchi-Tottoli apparatus and are not corrected. Microanalyses were done by the CNRS, Lyon. Optical rotations were determined in  $CH_2Cl_2$  solution at room temperature on a Perkin-Elmer Model 141 spectropolarimeter. Circular dichroism (CD) curves were recorded in methanol solution on a Jouan 3 dichrograph.

**Preparation of Alcohols 5.** Preparation of alcohols **5a** and **5c** has been previously described. Alcohol **5b** was secured by an adaptation of the same method.

**(R)-(-)-Cyclononen-2-ol.** 1,2-Cyclononadiene (7.3 g,  $6 \times 10^{-2}$  mol, obtained from cyclooctene<sup>21</sup>) was slowly added to  $Hg(OAc)_2$  (750 mg) in 85% formic acid (400 mL).<sup>22</sup> The reaction was monitored by TLC. After overnight stirring, the mixture was poured into aqueous  $K_2CO_3$ , extracted ( $Et_2O$ ), and worked up as usual. The crude liquid was purified by  $SiO_2$  chromatography to yield 8 g (80%) of *cis*-2-cyclononenyl formate: IR (film) 1730, 1660, 1170  $cm^{-1}$ ; NMR ( $CDCl_3$ )  $\delta$  7.9 (s, 1 H), 6.2–5.6 (m, 3 H), 2.5–1.0 (m, 12 H). Anal. ( $C_{10}H_{16}O_2$ ) C, H. A 5-g ( $3 \times 10^{-2}$  mol) sample of the preceding ester was treated with alcoholic KOH to yield 3.8 g (91%) of racemic 2-cyclononenol.<sup>22</sup> Camphanic ester was prepared by the described procedure from 3.55 g ( $2.53 \times 10^{-2}$  mol) of the alcohol and 5.64 g ( $2.6 \times 10^{-2}$  mol) of camphanic acid chloride. The diastereomeric mixture was crystallized four times from pentane to yield 860 mg of pure (-)-2-cyclononenyl camphanate: mp 102–103 °C;  $[\alpha]_D^{20}$  -69.5°; IR ( $CCl_4$ ) 3080, 1780, 1740, 1720  $cm^{-1}$ ; NMR ( $CDCl_3$ )  $\delta$  5.6 (m, 3 H), 2.5–1.2 (m, 16 H), 1.15 (s, 3 H), 1.05 (s, 3 H), 1.00 (s, 3 H). Anal. ( $C_{19}H_{28}O_4$ ) C, H. Cleavage of the ester (840 mg) with  $LiAlH_4$  in  $Et_2O$  at -20 °C yielded 330 mg (95%) of *cis*-(R)-(-)-2-cyclononenol,  $[\alpha]_D^{20}$  -41°.

**(R,aR)-(+)-Cyclodeca-2,3-dien-1-ol.** (-)-*cis*-2-Cyclononenol was transformed to (+)-cyclodeca-2,3-dien-1-ol by the procedure described previously.<sup>15</sup>

10,10-Dibromobicyclo[7.1.0]decan-2-ol: IR (film) 3400, 2930, 1450, 1030, 750  $cm^{-1}$ ; NMR ( $CDCl_3$ )  $\delta$  3.7 (m, 1 H), 2.0–1.0 (m, 14 H). Anal. ( $C_{10}H_{16}OBr_2$ ) C, H, Br.  $[\alpha]_D$ : -31°.

The trimethylsilyl ether of the alcohol has the following constants: IR (film) 2950, 1460, 1420, 1380, 1250  $cm^{-1}$ ; NMR ( $CDCl_3$ )  $\delta$  3.5 (m, 1 H), 1.9–1.6 (m, 14 H), 0.1 (s, 9 H). Anal. ( $C_{13}H_{24}OSiBr_2$ ) C, H, Br; calcd 41.67; found, 41.25.  $[\alpha]_D$ : -23.5°.

**(R,aR)-(+)-Cyclodeca-2,3-dien-1-ol trimethylsilyl ether:** IR (film) 1955, 1250  $cm^{-1}$ ; NMR ( $CDCl_3$ )  $\delta$  5.0 (m, 2 H), 4.3 (m, 1 H), 2.3–1.0 (m, 12 H), 0.2 (s, 9 H). Anal. ( $C_{13}H_{24}OSi$ ) C, H.  $[\alpha]_D$ : -8.5°.

**(R,aR)-(+)-Cyclodeca-2,3-dien-1-ol:** IR (film) 3350, 1955  $cm^{-1}$ ; NMR ( $CDCl_3$ )  $\delta$  5.1 (m, 2 H), 4.4 (m, 1 H), 2.35 (s, 1 H), 2.2–1.0 (m, 12 H);  $[\alpha]_D$  +27°; CD (MeOH) 222 nm;  $[\theta]$  -585.

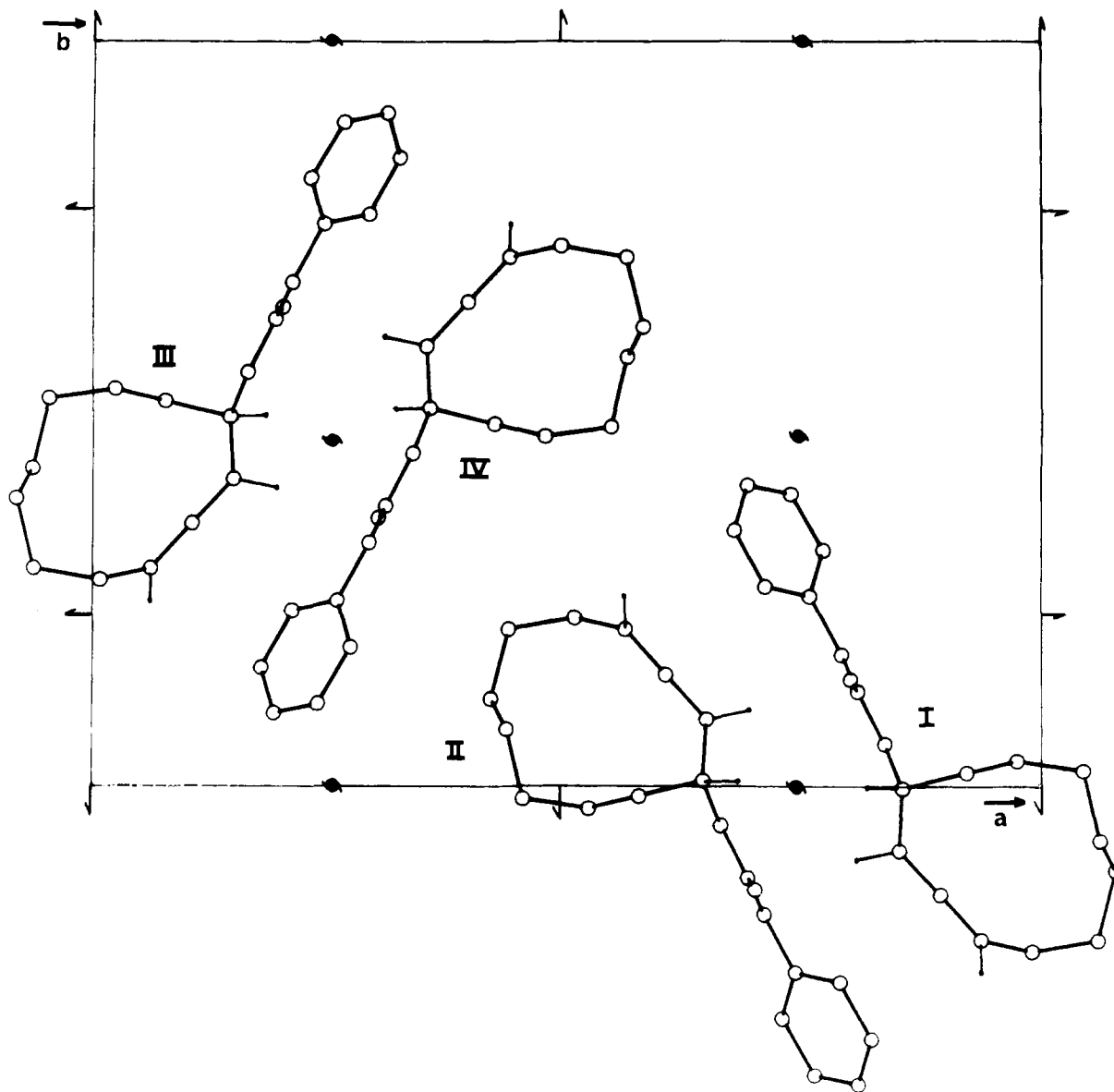
**Phenylurethanes 7.** **7a** in the racemic form has been described previously.<sup>1</sup> Optically active **7a** was prepared by the same procedure from **(R,aR)-(+)-cyclonona-2,3-dien-1-ol**.<sup>1</sup> Physical data of the racemate and optically active **7a** are the same except for melting point (87–87.5 °C) and optical rotation ( $[\alpha]_D$  +242°).

**7b** was obtained from the corresponding **(R,aR)-(+)-cyclodeca-2,3-**

(20) M. Cesario, J. Guilhem, C. Pascard, A. Collet, and J. Jacques, *Nouveau J. Chim.*, **2**, 343 (1978).

(21) L. Skattebol, *Acta Chem. Scand.*, **17**, 1683 (1963).

(22) (a) G. H. Whitham and M. Zaidlewicz, *J. Chem. Soc., Perkin Trans. 1*, 1509 (1972); (b) M. Santelli, M. Bertrand, and M. Ronco, *Bull. Soc. Chim. Fr.*, 3273 (1964).



**Figure 7.** Compound 7c: molecular packing along  $\bar{c}$ . I,  $(x, y, z)$ ; II,  $(\frac{3}{2} - x, -y, \frac{1}{2} + z)$ ; III,  $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$ ; IV,  $(x - \frac{1}{2}, \frac{1}{2} - y, -z)$ .

dien-1-ol: mp 89–90 °C (petroleum ether); IR (CCl<sub>4</sub>) 3330, 1960, 1710, 1540 cm<sup>-1</sup>; UV (EtOH) 236 nm ( $\epsilon$  19 800), 264 (4400), 272 (4420), 280 (2900); NMR (CDCl<sub>3</sub>)  $\delta$  7.5–6.8 (m, 5 H), 6.80 (s, 1 H), 5.7–4.8 (m, 3 H), 2.5–0.9 (m, 12 H). Anal. (C<sub>17</sub>H<sub>21</sub>O<sub>2</sub>N) C, H, N.  $[\alpha]_D^{25}$ : -11.5°. CD 228 nm  $[\theta]$  -25 500.

7c was obtained from cycloundeca-2,3-dien-1-ol, either racemic or the (*R,R*)-(+)-enantiomer. Both phenylurethanes show the same physical data: mp 93–93.5 °C (petroleum ether); IR (CCl<sub>4</sub>) 3320, 1950, 1700, 1535 cm<sup>-1</sup>; UV (EtOH) 234 nm ( $\epsilon$  16 200), 264 (3100), 272 (3300), 280 (2380); NMR (CCl<sub>4</sub>)  $\delta$  7.7–6.8 (m, 5 H), 6.5 (s, 1 H), 5.4–5.0 (m, 3 H), 2.5–1.0 (m, 14 H). Anal. (C<sub>18</sub>H<sub>23</sub>NO<sub>2</sub>) C, H, N.  $[\alpha]_D^{25}$ : +12.6°. CD 233 nm  $[\theta]$  -2900.

(*R*)-(+)-Cycloundeca-2,3-dien-1-one (4b). As described previously, MnO<sub>2</sub> oxidation of allenol furnished the corresponding ketone in 30% yield: IR (film) 1950, 1680 cm<sup>-1</sup>; UV (EtOH) 224 nm ( $\epsilon$  5250); NMR (CDCl<sub>3</sub>)  $\delta$  5.6 (m, 2 H), 2.5–1.0 (m, 12 H); MS *m/e* 150 (M<sup>+</sup>);  $[\alpha]_D^{25}$  + 68°,  $[\alpha]_{578}^{25}$  + 70.6°,  $[\alpha]_{545}^{25}$  + 77.5°,  $[\alpha]_{436}^{25}$  + 93°,  $[\alpha]_{365}^{25}$  - 225°; CD 222  $[\theta]$  + 16 040, 253  $[\theta]$  - 15 200, 307  $[\theta]$  + 174, 337 nm  $[\theta]$  - 660.

**X-ray Data Structure Determinations.** Suitable crystals (0.3–0.4 mm parallelepipeds) of compounds 7 were grown by slow evaporation of a hexane or petroleum ether solution at 4 °C. Cell parameters were refined from measurements collected with four-circle Siemens and CAD4 Nonius automatic diffractometers,<sup>23</sup> with copper K $\alpha$  radiation. Intensities were

measured with a  $\theta$ - $2\theta$  scanning by the five points method<sup>24</sup> or the step by step method.

Structures were solved by a direct multisolution technique<sup>25</sup> and refined with a full-matrix least-squares method<sup>26</sup> minimizing the quantity  $\sum (F_o - F_c)^2$ . Coordinates and anisotropic thermal factors expressed by  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$  were varied for C, O, and N atoms. Calculated coordinates and isotropic thermal factors were kept constant for the hydrogens. A weighting law was obtained from the curve  $w(F_o - F_c)^2$  vs.  $F_o$ . The weighted residual factors expressed by  $R = [w(F_o - F_c)^2 / F_o^2]^{1/2}$  are given in Table I. Coordinates, thermal parameters, and calculated and observed structure factors are given in the microfilm edition, together with bond distances and angles for compounds 7b and 7c (the corresponding data for 7a have been published previously<sup>1</sup>).

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**Supplementary Material Available:** Atomic coordinates, thermal parameters, and tables of structure factors, bond lengths, and angles (47 pages). Ordering information is given on any current masthead page.

(23) Measurements were made at the Institut Laue-Langevin and the Laboratoire des Rayons-X, CNRS, Grenoble, France. All the calculations were made with an IRIS-80 computer.

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