Dimethyldecodine showed (c 0.186) $[\theta]_{3025}$ 0, $[\theta]_{2900}$ $-15{,}568$, $[\theta]_{2650}$ -486, $[\theta]_{2400}$ $-20{,}246$, $[\theta]_{2200}$ $-97{,}300$, $[\theta]_{2100}$ 0, $[\theta]_{2000}$ $+238{,}385$, $[\theta]_{1925}$ $+116{,}760$.

Vertine showed (c 0.072) $[\theta]_{3225}$ 0, $[\theta]_{3100}$ $-60{,}480$, $[\theta]_{3025}$ 0, $[\theta]_{2825}$ $+287{,}280$, $[\theta]_{2400}$ 0, $[\theta]_{2225}$ $-1{,}285{,}200$, $[\theta]_{2125}$ 0, $[\theta]_{2025}$ $+145{,}200$, $[\theta]_{1925}$ $+48{,}400$.

Emde methyldecinine showed (c 0.2) $[\theta]_{3075}$ 0, $[\theta]_{2875}$ $-18{,}704$, $[\theta]_{2650}$ -7949, $[\theta]_{2475}$ $-21{,}509$, $[\theta]_{2400}$ 0, $[\theta]_{2300}$ $+88{,}844$, $[\theta]_{2238}$ 0, $[\theta]_{2150}$ $-112{,}224$, $[\theta]_{2075}$ 0, $[\theta]_{2025}$ $+149{,}632$, $[\theta]_{1950}$ $+74{,}816$.

Emde methyldecamine showed (c 0.41) $[\theta]_{3050}$ 0, $[\theta]_{2875}$, $-22{,}810$, $[\theta]_{2650}$ -6843, $[\theta]_{2475}$ $-27{,}372$, $[\theta]_{2400}$ 0; (c 0.205) $[\theta]_{2300}$ $+86{,}678$, $[\theta]_{2238}$ 0, $[\theta]_{2150}$ $-123{,}174$, $[\theta]_{2075}$ 0, $[\theta]_{2000}$ $+187{,}042$, $[\theta]_{1950}$ $+68{,}430$.

Lythridine showed (c 0.136) $[\theta]_{3075}$ 0, $[\theta]_{2800}$ $-30{,}015$, $[\theta]_{2600}$ $-10{,}005$, $[\theta]_{2475}$ $-20{,}010$, $[\theta]_{2400}$ 0, $[\theta]_{2325}$ $+33{,}350$, $[\theta]_{2285}$ 0, $[\theta]_{2175}$ $-133{,}400$, $[\theta]_{2100}$ 0, $[\theta]_{2000}$ $+ 240{,}120$, $[\theta]_{1950}$ $+106{,}720$.

Methyllagerine showed (c 0.126) $[\theta]_{2975}$ 0, $[\theta]_{2900}$ $+6994$, $[\theta]_{2850}$ $+5208$, $[\theta]_{2725}$ $+20{,}832$, $[\theta]_{2475}$ 0, $[\theta]_{2300}$ $-105{,}896$, $[\theta]_{2200}$ 0, $[\theta]_{2150}$ $+27{,}776$, $[\theta]_{2125}$ 0, $[\theta]_{2000}$ $-361{,}140$, $[\theta]_{1925}$ 0.

Decaline showed (c 0.108) $[\theta]_{3100}$ 0, $[\theta]_{2950}$ $+48{,}600$, $[\theta]_{2815}$ 0, $[\theta]_{2750}$ $-38{,}475$, $[\theta]_{2575}$ 0, $[\theta]_{2475}$ $+22{,}275$, $[\theta]_{2400}$ 0, $[\theta]_{2275}$ $-109{,}350$, $[\theta]_{2150}$ $-22{,}275$, $[\theta]_{2000}$ $-194{,}400$, $[\theta]_{1950}$ $-97{,}200$.

Vertaline showed (c 0.036) $[\theta]_{3075}$ 0, $[\theta]_{2950}$ $+43{,}758$, $[\theta]_{2820}$ 0, $[\theta]_{2750}$ $-38{,}896$, $[\theta]_{2575}$ 0, $[\theta]_{2475}$ $+19{,}448$, $[\theta]_{2400}$ 0, $[\theta]_{2250}$ $-109{,}395$, $[\theta]_{2125}$ $-29{,}172$, $[\theta]_{2000}$ $-145{,}848$, $[\theta]_{1975}$ $-103{,}309$.

Neodihydrothebaine showed (c 0.157) $[\theta]_{2975}$ 0, $[\theta]_{2750}$ $+4991$, $[\theta]_{2625}$ 0, $[\theta]_{2450}$ $-11{,}978$, $[\theta]_{2325}$ 0, $[\theta]_{2150}$ $-79{,}840$, $[\theta]_{2080}$ 0, $[\theta]_{2000}$ $+263{,}472$, $[\theta]_{1950}$ $+139{,}720$.

α-Methyldihydrothebaine perchlorate showed (c 0.076) $[\theta]_{3050}$ 0, $[\theta]_{2800}$ $+10{,}130$, $[\theta]_{2575}$ 0, $[\theta]_{2450}$ -6753, $[\theta]_{2375}$ 0, $[\theta]_{2325}$ $+11{,}260$, $[\theta]_{2300}$ 0; (c 0.25) $[\theta]_{2150}$ $-153{,}990$, $[\theta]_{2075}$ 0, $[\theta]_{2000}$ $+359{,}310$, $[\theta]_{1950}$ $+136{,}880$.

η-Methyldihydrothebaine perchlorate showed (c 0.17) $[\theta]_{3025}$ 0, $[\theta]_{2775}$ -5031, $[\theta]_{2575}$ 0, $[\theta]_{2525}$ $+1509$, $[\theta]_{2450}$ 0, $[\theta]_{2325}$ $-25{,}155$, $[\theta]_{2265}$ 0, $[\theta]_{2150}$ $+55{,}341$, $[\theta]_{2090}$ 0, $[\theta]_{2025}$ $-186{,}147$, $[\theta]_{1975}$ $-60{,}372$.

Optical Rotatory Dispersion Measurements. The ORD measurements were carried out in methanol solution using a Cary Model 60 spectropolarimeter and are recorded in units of molecular rotation.

Compound VIa[25] showed $[\alpha]_{350}$ $-260°$, $[\alpha]_{330}$ $-360°$, $[\alpha]_{300}$ $-480°$, $[\alpha]_{280}$ $-720°$, $[\alpha]_{250}$ $-1020°$, $[\alpha]_{240}$ $-1350°$.

Compound VIb[25] showed $[\alpha]_{350}$ $+160°$, $[\alpha]_{330}$ $+220°$, $[\alpha]_{300}$ $+410°$, $[\alpha]_{280}$ $+410°$, $[\alpha]_{250}$ $+730°$, $[\alpha]_{240}$ $+1240°$.

Acknowledgments. We wish to thank Mr. Roger Williams, University of California (Berkeley), and Mr. Norman Mitchell, Applied Physics Corporation, for measuring the ORD spectra of some of these alkaloids. We acknowledge the use of the Cary 60 spectropolarimeter at Harvard University for the measurement of the ORD spectra of VI. We thank Dr. K. W. Bentley for a sample of neodihydrothebaine, Drs. E. L. May and L. J. Sargent of NIH for making available the methyldihydrothebaines from the collection of the late Dr. L. Small, and Dr. A. E. Schwarting for a sample of lythridine.

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(25) The molecular rotations reported for VIa and VIb are of limited accuracy due to the intense uv absorption, the low molecular rotation, and the small amounts of these compounds. However, it is clear that the curves are of opposite sign. There may be a weak Cotton effect at 285 nm; however, this is not certain for the above-mentioned reasons.

Optical Properties of Some Heterohelicenes. The Absolute Configuration

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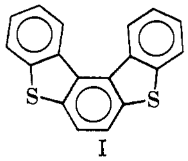
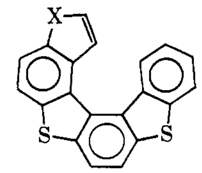
Received August 29, 1970

Abstract: The electronic spectra of a number of heterohelicenes are discussed. The optical rotatory dispersion and circular dichroism spectra of the resolved ones were measured. Calculations on a model compound were performed to establish the absolute configuration. The right-handed chirality was assigned to the (+)-heterohelicenes.

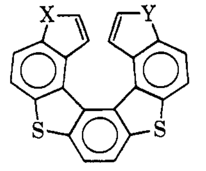
In previous papers we described the synthesis and resolution of a number of heterohelicenes[1] (I-VII). With the exception of I, IV, and VI these compounds were obtained in an optically active form, mainly by crystal picking, and they were found to show very high optical rotations due to the presence of an inherently dissymmetric chromophore.[2] In order to study this phenomenon in more detail we measured the optical rotatory dispersion (ORD) and circular dichroism (CD) spectra of the resolved heterohelicenes. Since these spectra cannot be interpreted well without knowledge of the uv spectra,[3] attention will be paid first to these spectra. Further objectives were (a) to assign the absolute configurations with the aid of the ORD and CD spectra and (b) to evaluate the effect of overcrowding on the uv spectra of the heterohelicenes. This work was



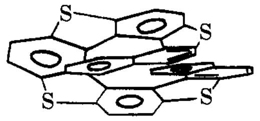
I



II, X = CH═CH
III, X = S



IV, X = Y = CH═CH
V, X = CH═CH; Y = S
VI, X = Y = S



VII

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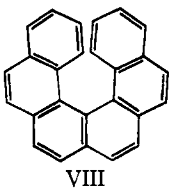
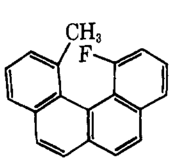
(1) (a) H. Wynberg and M. B. Groen, *J. Amer. Chem. Soc.*, **90**, 5339 (1968); (b) H. Wynberg and M. B. Groen *ibid.*, **92**, 6664 (1970); (c) M. B. Groen, G. Stulen, G. J. Visser, and H. Wynberg, *ibid.*, **92**, 7218 (1970).

(2) A. Moscowitz, *Tetrahedron*, **13**, 48 (1961); Ph.D. Thesis, Harvard University, Cambridge, Mass., 1957.

(3) In some cases including the visible region.

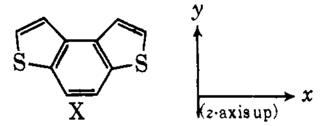
stimulated by the fact that in spite of a great deal of effort the absolute configuration problem of hexahelicene VIII has not been solved unambiguously. Several attempts have been made to establish the absolute configuration of compound[2,4] VIII, the synthesis and resolution of which were described by Newman.[5] Most workers predicted the isomer with right-handed chirality to be dextrorotatory, but Moscowitz, on the basis of HMO calculations, arrived at the opposite conclusion. Similar calculations have been performed by Kemp and Mason to derive the absolute configuration of a tetrahelicene, 1-fluoro-12-methylbenzo[*c*]phenanthrene (IX), from its CD spectrum.[6] We hoped that the ORD and CD spectra of the heterohelicenes would show sufficient resemblance to the spectra of the benzenoid helicenes to allow the interrelation of their respective configurations. Experimental proof of the absolute configuration of only one of these compounds would then fix that of all the others. Such semiempirical correlations have been proven to be very useful for various classes of dissymmetric compounds, *i.e.*, twisted bridged diphenyls,[7] twisted dienes,[8] α,β-unsaturated ketones,[9] etc.


VIII



IX

It turned out, however, that the CD and ORD spectra of the heterohelicenes under study were quite different from those of hexahelicene and the compound IX. The spectra suggested that the sign and magnitude of the long-wavelength optical rotation is somewhat arbitrary and fortuitous, being the result of various optically active electronic transitions. In our opinion the method used by Moscowitz and Mason, which predicts for a given configuration of a helicene both sign and strengths of selected Cotton effects or CD bands, is a more reliable tool to determine the absolute configuration of such a compound than the methods in which only the long-wavelength rotation is considered. We found that the relative signs and magnitudes of the three lowest energy CD bands of the heterohelicenes were in good agreement with those obtained for a simplified model compound, namely helically distorted benzo[1,2-*b*:4,3-*b*′]dithiophene (X). The choice of such a model seemed justified by the remarkable similarity of both the uv and the CD spectra within the group of compounds under study. Our results strongly suggest that the (+)-heterohelicenes described here have the configuration of a right-handed helix.[10]



X

Results and Discussion

Uv Spectra. The uv spectra of the heterohelicenes I–VII are drawn in Figure 1. They show resolved bands and vibrational structure, which is in marked contrast to the uv spectra reported of hexahelicene and its benzologs hepta-,[11] octa-,[12] nona-,[12] and tridecahelicene.[13] In these spectra the fine structure is blurred and the different bands can be located only with difficulty.[14] The loss of fine structure might be attributed to the overcrowding in the molecule, but this does not explain why in the equally overcrowded heterohelicenes this loss of fine structure is so much less pronounced. Further striking features which follow from Figure 1 are the close mutual resemblance of the spectra of the two hexahelicenes II and III and the three heptahelicenes IV, V, and VI and the structural similarity of all spectra; on the long-wavelength side of the spectra of I, II, and III a relatively weak band (log $\epsilon \approx 4$) is found, followed by a stronger band (log $\epsilon \approx 4.5$), and again a weaker band (log $\epsilon \approx 4$). At still shorter wavelengths very strong bands are found (log ϵ up to 5). In the higher helicenes the first band has disappeared (hidden by the second band), whereas the intensity of the third band has increased. This tentative interpretation was confirmed by the CD spectra as will be seen later. Weigang and coworkers[14b] have shown that the uv spectrum of hexahelicene could be interpreted with the aid of a diagram correlating the different bands in the spectra of benzene,

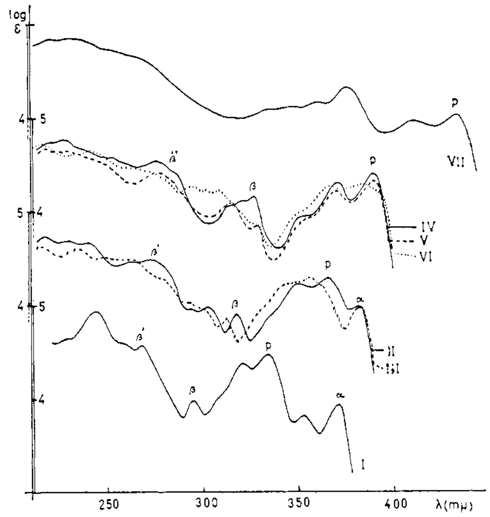


Figure 1. The uv spectra of the heterohelicenes (cyclohexane).

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(4) (a) D. D. Fitts and J. G. Kirkwood, *J. Amer. Chem. Soc.*, 77, 4940 (1955); (b) I. Tinoco and R. W. Woody, *J. Chem. Phys.*, 40, 160 (1964); (c) R. Brewster, *Top. Stereochem.*, 2, 40 (1967).

(5) (a) M. S. Newman and D. Lednicer, *J. Amer. Chem. Soc.*, 78, 4765 (1956); (b) M. S. Newman, R. S. Darlak, and L. Tsai, *ibid.*, 89, 6191 (1967).

(6) C. M. Kemp and S. F. Mason, *Tetrahedron*, 22, 629 (1966).

(7) K. Mislow, *Ann. N. Y. Acad. Sci.*, 93, 459 (1962).

(8) A. Moscowitz, E. Charney, W. Weiss, and H. Ziffer, *J. Amer. Chem. Soc.*, 83, 4661 (1961).

(9) C. Djerassi, R. Records, E. Bannenberg, K. Mislow, and A. Moscowitz, *ibid.*, 84, 870 (1962).

(10) Attempts to determine the absolute configuration of II by this method have been carried out by G. Stulen and G. J. Visser (Laboratorium voor Structuurchemie, Professor D. A. Vos). After the completion of this manuscript the successful results became available (to be published). The X-ray results confirm the assignments of the absolute configurations made in this paper.

(11) M. Flammang-Barbieux, J. Nasielski, and R. H. Martin, *Tetrahedron Lett.*, 743 (1967).

(12) R. H. Martin, H. Flammang-Barbieux, J. P. Cosijn, and M. Gelbcke, *ibid.*, 3507 (1968).

(13) R. H. Martin, G. Morren, and J. J. Schurter, *ibid.*, 3683 (1969).

(14) This has led to an erroneous interpretation of the uv spectrum of hexahelicene: (a) W. Rhodes and M. F. El-Sayed, *J. Mol. Spectrosc.*, 9, 42 (1962). The spectrum could be analyzed, however, by polarization measurements; (b) O. E. Wolfgang, J. A. Turner, and P. A. Trouard, *J. Chem. Phys.*, 45, 1126 (1966).

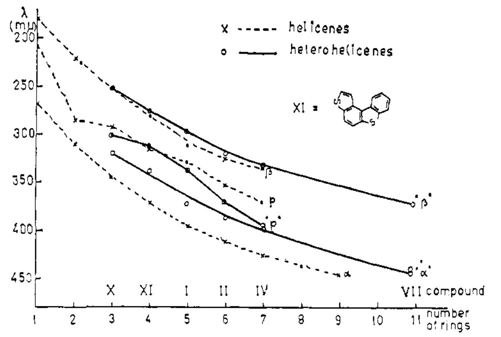

Figure 2. Diagram representing the position of the three longest wavelength bands of the helicenes and some heterohelicenes.

naphthalene, phenanthrene,[15] etc., up to hexahelicene. Similarly a series of heterohelicenes can be constructed starting with benzo[1,2-*b*:4,3-*b*′]dithiophene (X). The diagram in Figure 2, which is a modified version of that used by Weigang, shows both series of helicenes. In this diagram the positions of the first distinct vibrational peak[16] of the three lowest energy uv bands are plotted against the total number of benzene and thiophene rings present in the molecule. The data for the helicenes were obtained from Clar[17] and van der Donakt, *et al.*;[18] other data are given in the Experimental Section. Inspection of the diagram shows that the heterohelicenes behave very similarly to the "ordinary" (containing only benzene rings) helicenes. If one of the thiophene compounds under study is compared with the corresponding benzene compound it turns out that the longest wavelength band (labeled α) is found systematically at a shorter wavelength (*ca.* 30 mμ) but the second and especially the third band (labeled p and β, respectively) often differ very little in their positions. The intensity of the first band is much higher and that of the third band much lower, however, in the thiophene series. In the helicene series the bands labeled α and β are on smooth curves, which are almost exactly parallel with a distance of 90 mμ, whereas the p bands are located on a zig-zag line. In the heterohelicenes the uv bands show the same trends, the distance between the first and third band being *ca.* 60 mμ. No sudden change in the curves in Figure 2 is observed as soon as overcrowding becomes important,[19] so there is no evidence that overcrowding affects the uv spectra of the heterohelicenes. We have tacitly adopted here the spectroscopic labeling system of Clar,[17] who was the first to point out the strong similarities between the uv spectra of a great variety of condensed aromatic hydrocarbons, all having in common the following characteristic bands in order of decreasing wavelength:[17] α (weak, consisting of sharp peaks), p (medium strong, log ϵ 4–5, usually at least three vibrational peaks), β, β', β'', etc. (strong bands, log ϵ 4–6, little fine structure). Although the uv bands of the heterohelicenes do not completely meet the criteria of Clar, the results as shown in Figure 2 strongly suggest that his classification can be used, with some reserve, for these compounds as well. The similarity in structure of the uv spectra of polycyclic hydrocarbons and their thiophene analogs has been noted previously and several examples are given in the literature.[20]

A qualitative understanding of the long-wavelength part of the uv spectra of aromatic hydrocarbons can be obtained from HMO theory. It turns out that the promotion of an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) gives rise to the p band. Because of the symmetric arrangement of bonding and antibonding energy levels in alternating hydrocarbons, the transitions next in energy, promotion of an electron from the HOMO to the lowest but one unoccupied molecular orbital or from the highest but one occupied molecular orbital to the LUMO, are degenerate. Configuration interaction leads to a high-energy allowed and a low-energy forbidden transition, resulting in the β and α bands, respectively. In condensed heterocyclic compounds the energy levels of the bonding and antibonding MO's are no longer symmetrically arranged. This has the following consequences. (a) Promotion of an electron from the HOMO to the LUMO still gives rise to a p band. (b) Configuration interaction is less drastic; therefore the split between the α-type band and the β-type band is smaller, which is in agreement with the experimental results. (c) Usually one configuration predominates in the α band, which is no longer forbidden, and another configuration predominates in the β band. Of course the picture given here is an oversimplification since second-order configuration interaction can affect a spectrum drastically, but it suffices for a qualitative understanding of the observed uv spectra.

ORD and CD Spectra. In Figures 3–5 the ORD spectra of (+)-II, (+)-III, and (+)-V are shown and in Figures 6–9 the CD spectra of the same compounds as well as that of (+)-VII are shown. The values of $\epsilon_l - \epsilon_r$ have to be considered as minimum values since some samples might be optically impure. The CD spectrum of (+)-VII has been corrected for the fact that the sample is at best 7% optically pure in order to facilitate comparison with the other CD spectra. We see that the ORD and CD spectra are quite similar in structure. The α band (not visible in the uv spectra of V and VII!) is always associated with a negative Cotton effect and a negative dichroism, whereas the p band, although strong in the uv spectra, gives rise to a weak, positive dichroism (the Cotton effects in the ORD spectra due to this band are unclear). The next two bands, β and β', give rise to strong positive dichroisms and the ORD spectra reveal that *these highly active bands govern the sign of the optical rotation in the visible region.* Finally all compounds show a strong negative dichroism at short wavelength. The ORD spectra were not measured in this region. We already note a principal difference with the optical properties of hexahelicene VIII at first glance: the ORD and CD spectra of the latter compound[5b,14b] clearly reveal that the strong Cotton effect associated with the p band governs the optical rotation in the visible region, whereas the α and β bands show almost negligible optical activity. Often

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(15) These compounds, although planar, can be considered as the lower members of the helicene series.

(16) This is somewhat arbitrary; more exact but more difficult in practice would be the location of 0–0 transition.

(17) E. Clar, "Polycyclic Hydrocarbons," Academic Press, London, 1964.

(18) E. van der Donakt, J. Nasielski, J. R. Greenleaf, and J. B. Birks, *Chem. Phys. Lett.*, 2, 409 (1968).

(19) As evidenced by optical activity.

(20) (a) C. M. Badger and B. J. Christie, *J. Chem. Soc.*, 3438 (1956); (b) W. Carruthers and R. J. Crowder, *ibid.*, 1932 (1957).

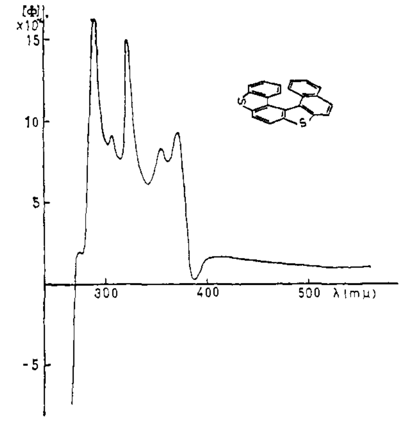

Figure 3. The ORD spectrum of (+)-II.

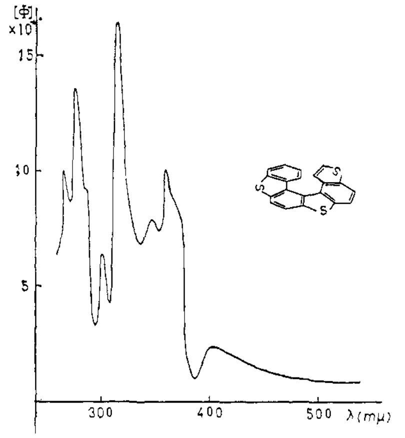

Figure 4. The ORD spectrum of (+)-III.

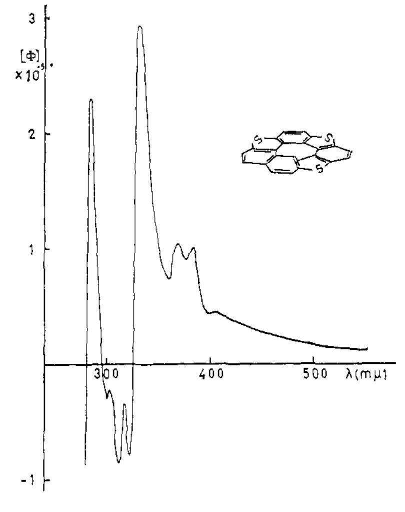

Figure 5. The ORD spectrum of (+)-V.

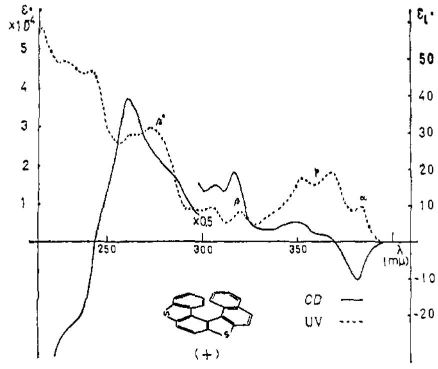

Figure 6. The CD spectrum of (+)-II.

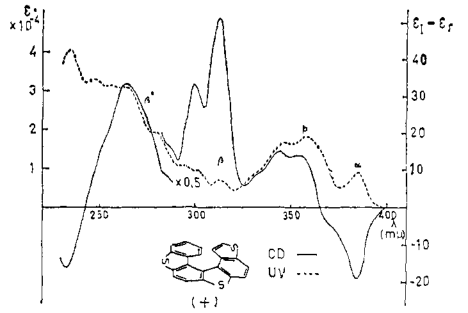

Figure 7. The CD spectrum of (+)-III.

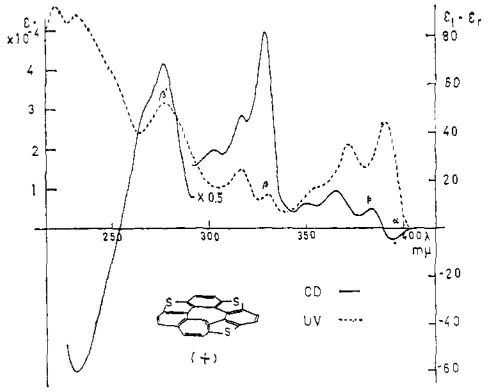

Figure 8. The CD spectrum of (+)-V.

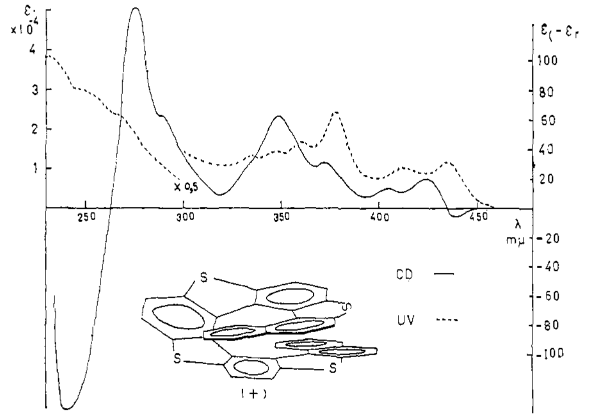

Figure 9. The CD spectrum of (+)-VII.

the shape of CD bands is very similar to the shape of the corresponding uv bands. The dissymmetry or anisotropy factor g which is defined as[21]

$$g = \frac{\epsilon_l - \epsilon_r}{\epsilon} \qquad (1)$$

is a constant in such cases within the band. Moffitt and Moscowitz[22] have pointed out that such behavior can be expected for the transitions of an inherently dissymmetric chromophore, which are both electrically and magnetically allowed. For weak bands, however, the

(21) W. Kuhn, *Trans. Faraday Soc*, **46**, 293 (1930).

(22) W. Moffitt and A. Moscowitz, *J. Chem. Phys.*, **30**, 648 (1959).

dichroism curves might be slightly red-shifted compared to the absorption curve and the anisotropy factor is not necessarily constant for the various vibronic sub bands.[23] Inspection of Figures 6–8 shows that there is a fair correspondence between the positive or negative maxima in the CD curves and the peaks in the uv spectra. The p bands seem slightly blue-shifted in the CD spectra; apart from solvent effects this is probably the result of the overlap with the negative CD associated with the α band. The strong overlap of the various bands might explain also the larger difference between the CD and uv spectra of VII as shown in Figure 9. Interestingly enough the β bands do not exhibit a constant anisotropy factor particularly in the case of V (Figure 8). The first vibrational peak (the 0–0 transition) is far strongest in the CD spectrum, whereas the second one is strongest in the uv spectrum. Theoretically this is to be expected for an electrically forbidden magnetically allowed transition.[22] The Cotton effects in the ORD spectra and the intensity of CD bands are governed by the quantum mechanical quantity R_{ba}, the rotational strength of the transition a → b, which experimentally can be calculated with the approximate relation

$$R_{\mathrm{ba}} = 0.23 \times 10^{-38} \int_0^{\infty} \frac{(\epsilon_{\mathrm{l}} - \epsilon_{\mathrm{r}})_{\mathrm{ba}}}{\lambda} \mathrm{d}\lambda \qquad (2)$$

R_{ba} is defined as the imaginary part of the scalar product of the electric and magnetic transition moment, $\vec{\epsilon}_{\mathrm{ab}}$ and $\vec{\mu}_{\mathrm{ab}}$, respectively[2] (eq 3). In molecules possessing no

$$R_{\mathrm{ba}} = Im(\vec{\epsilon}_{\mathrm{ab}},\vec{\mu}_{\mathrm{ba}}) = |\vec{\epsilon}_{\mathrm{ab}}||\vec{\mu}_{\mathrm{ba}}| \cos \alpha \qquad (3)$$

dissymmetry, $\vec{\mu}_{\mathrm{ba}}$ is either zero or at right angles with $\vec{\epsilon}_{\mathrm{ab}}$ (consequently $\cos \alpha = 0$) with the result that there is no optical activity. In dissymmetric molecules, $\vec{\mu}_{\mathrm{ba}}$ has an appreciable component in the direction of $\vec{\epsilon}_{\mathrm{ab}}$, particularly in the helicenes, where all $\pi \rightarrow \pi^*$ transitions involve displacement of electronic charge through a more or less helical path. Calculation of R_{ba} with simple HMO theory raised several problems, *e.g.*, the values of R_{ba} were found to be dependent on the choice of the origin, but these problems were overcome by Moscowitz[2] using the so-called dipole velocity method. This method has been applied by Moscowitz for hexahelicene VIII and by Kemp and Mason[6] for 1-fluoro-12-methylbenzo[*c*]phenanthrene (IX). In both cases the helicene with right-handed chirality (the P configuration[24]) was calculated to have a negative dichroism (and Cotton effect) associated with the p band. Experimentally this was shown to be so for (−)-hexahelicene and (+)-IX. In the latter case the positive optical rotation in the visible region is caused by the strong positive Cotton effect associated with the β band, which overshadows that of the p band, and in this respect the heterohelicenes behave much more like IX than like hexahelicene.

Absolute Configuration. Since the CD spectra of the heterohelicenes were all very similar, it seemed reasonable that the benzo[1,2-*b*:3-*b*′]dithiophene moiety, which is common to all these compounds, plays an important role. We therefore took helically distorted benzo[1,2-*b*:4,3-*b*′]dithiophene (X) as a model compound and applied the dipole velocity method to this imaginary compound.[25] Benzo[1,2-*b*:4,3-*b*′]dithiophene (X) has seven bonding and seven antibonding π orbitals. In planar benzo[1,2-*b*:4,3-*b*′]dithiophene the transition $\psi_7 \rightarrow \psi_8$, which gives rise to the p band, is polarized along the axis, whereas the transitions $\psi_6 \rightarrow \psi_8$ and $\psi_7 \rightarrow \psi_9$, leading to the α and β band, are y polarized (along the C_2 axis). Furthermore, it can be seen from symmetry considerations that only the transition $\psi_7 \rightarrow \psi_8$ has a magnetic moment, which is perpendicular to the plane of the molecule (z polarized). The molecule can be distorted in such a way that a segment of a helix is formed with retention of the C_2 axis (along the y axis). The result of this operation is that the transitions $\psi_6 \rightarrow \psi_8$ and $\psi_7 \rightarrow \psi_9$ get a magnetic moment in the y direction and therefore these transitions become optically active. The transition $\psi_7 \rightarrow \psi_8$ is a more complex case; the transition gets a magnetic moment in the x direction, but also an electric moment in the z direction. Consequently, there are two contributions to the rotational strength of this transition. We chose for our calculations a right-handed helicity of the molecule. The coordinates of the atoms and bonds needed for the computations were estimated from a model of II based on its X-ray analysis.[26]

The procedure has been described elsewhere[6] and only a few remarks will be made here. Rather than the rotational strength, we calculated the dissymmetry factor g of the various transitions which is approximated by

$$g = 4\pi\bar{\nu}_{\mathrm{ba}} \frac{(\psi_{\mathrm{a}}|\vec{\nabla}|\psi_{\mathrm{b}})(\psi_{\mathrm{a}}|\vec{\mathrm{r}}\,\vec{\nabla}|\psi_{\mathrm{b}})}{|(\psi_{\mathrm{a}}|\vec{\nabla}|\psi_{\mathrm{b}})|^2} \qquad (4)$$

In this equation $\bar{\nu}_{\mathrm{ba}}$ = the frequency of the transition $\psi_{\mathrm{a}} \rightarrow \psi_{\mathrm{b}}$ (in reciprocal centimeters). Evaluation of the elements $(\psi_{\mathrm{a}}|\vec{\mathrm{r}}\vec{\nabla}|\psi_{\mathrm{b}})$ and $(\psi_{\mathrm{a}}|\vec{\nabla}|\psi_{\mathrm{b}})$, to which, respectively, the magnetic and electric transition moments $\vec{\mu}_{\mathrm{ab}}$ and $\vec{\epsilon}_{\mathrm{ab}}$ are proportional, in the LCAO approximation requires the calculation of the so-called transitional bond-order changes, which were obtained with the PPP–SCF method.[25] Furthermore, one has to calculate the dipole velocity elements $\vec{\nabla}_{\mathrm{rs}}$

$$\vec{\nabla}_{\mathrm{rs}} = \int \phi_{\mathrm{r}}\vec{\nabla}_{\mathrm{s}} \qquad (5)$$

The element $\vec{\nabla}_{\mathrm{rs}}$ is a vector directed along the bond between the atoms r and s in the direction r → s. ϕ_{r} and ϕ_{s} are atomic orbitals. Its expectation value $\langle\nabla_{\mathrm{rs}}\rangle$ has been derived both theoretically and empirically for the aromatic carbon–carbon π bond by Moscowitz.[2] One can derive that $\langle\nabla_{\mathrm{rs}}\rangle$ must be equal to the gradient of the overlap integral S along the bonds (if ϕ_{r} and ϕ_{s} are π orbitals). Using the Linderberg relation[27] one obtains a very simple expression for the dipole velocity element[28]

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(23) This is clearly the case for the α band of hexahelicene as is revealed by its low-temperature uv and CD spectra (O. E. Weigang, Jr., and P. A. Trouard Dodson, *ibid.*, 49, 4248 (1968).

(24) R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, 5, 385 (1966).

(25) The synthesis and properties of X have been described (R. M. Kellogg, M. B. Groen, and H. Wynberg, *J. Org. Chem.*, 32, 3093 (1967)). PPP–SCF calculations of the electronic properties of this compound were performed by Mr. J. B. Roedelof (Laboratorium voor Theoretische Chemie, Professor E. H. Wiebenga), providing the data for the calculations described here. It is the helical distortion of X which is considered as an imaginary process, although such a distortion actually might be brought about by proper substitution of X with bulky groups.

(26) G. Stulen and G. J. Visser, *Chem. Commun.*, 964 (1969).

(27) J. Linderberg, *Chem. Phys. Lett.*, 1, 39 (1967).

(28) This was suggested to us by Dr. D. Kracht (Laboratorium voor Theoretische Chemie, Professor W. C. Nieuwpoort).

Table I. The Elements $(\psi_a|\vec{\nabla}|\psi_b)$ and $(\psi_a|\vec{r}\,\vec{\nabla}|\psi_b)$ and the Dissymmetry Factor g of the Three Lowest Energy Transitions

Transition	$(\psi_a\|\vec{\nabla}\|\psi_b)$ (in $\langle\nabla_{cc}\rangle$)			$(\psi_a\|\vec{r}\,\vec{\nabla}\psi_b)$ (in $\langle\nabla_{cc}\rangle \times$ Å)			
	x	y	z	x	y	z	g
$\psi_7 \rightarrow \psi_8$	−1.088	0	−0.024	−0.011	0	+0.660	0
$\psi_6 \rightarrow \psi_8$	0	−0.720	0	0	+0.237	0	−0.001
$\psi_7 \rightarrow \psi_9$	0	−0.587	0	0	−0.132	0	+0.001

$$\langle\nabla_{rs}\rangle = \frac{dS}{dR} = R\beta \tag{6}$$

where R = the length of the bond rs and β = resonance integral (both in atomic units). Assuming $\beta_{cs} = 0.6\beta_{cc}$,[29] $R_{cc} = 1.40$ Å, and $R_{cs} = 1.72$ Å it can easily be seen that $\langle\nabla_{cs}\rangle = 0.74\langle\nabla_{cc}\rangle$, where $\langle\nabla_{cs}\rangle$ is the dipole velocity element for the carbon-sulfur bond in a thiophene ring and $\langle\nabla_{cc}\rangle$ is that for an aromatic carbon-carbon bond.[30] The elements $(\psi_a|\vec{\nabla}|\psi_b)$ and $(\psi_a|\vec{r}\,\vec{\nabla}|\psi_b)$ expressed in $\langle\nabla_{cc}\rangle$ as an atomic unit and the dissymmetry factor g for the various transitions are represented in Table I.

It turns out that for the transition $\psi_7 \rightarrow \psi_8$, the contributions to the rotational strength (ϵ_x, μ_x and ϵ_z, μ_z) are small and opposite in sign. They, therefore, mutually cancel and the resulting activity is expected to be very low. The transition $\psi_6 \rightarrow \psi_8$ has a negative and the transition $\psi_7 \rightarrow \psi_9$ a positive rotational strength; with formula 4 (setting $\bar{\nu} = 3.33 \times 10^{-4}$ Å) it is easily found that the value of g is -1.0×10^{-3} and $+1.0 \times 10^{-3}$, respectively. Slight variations of the assumed geometry did not change these results materially. Since the transition $\psi_6 \rightarrow \psi_8$ contributes most strongly to the α band and the transition $\psi_7 \rightarrow \psi_9$ to the β band,[31] it is plausible that these bands show a negative and a positive circular dichroism, respectively. No attempts were made, however, to refine the calculations by taking configuration interaction into account.[32] The calculations performed should apply directly to a molecule like 1,8-di-*tert*-butylbenzo[1,2-*b*:4,3-*b*′]dithiophene, the synthesis of which is currently attempted. The strong similarity of the CD spectra of the heterohelicenes suggests that anellation does not change the optical properties of the system significantly and at least qualitatively the results obtained here should also hold for the higher helicenes. In any case, the agreement between the calculations and the observed CD spectra is remarkable: the α and β bands show dichroisms of opposite sign and the optical activity of the p band is very low indeed. *We therefore conclude that the* (+)-*heterohelicenes described in this paper have a right-handed helicity* (or a P configuration[24]). This means that the (+)-heterohelicenes have the same configuration as (+)-IX and (−)-hexahelicene, if the assignments made by Moscowitz,[2] by Kemp and Mason,[6] and by us are correct. Experimental support (although not to be taken as strong evidence) for this statement is found in the fact that (+)-2-(2,4,5,7-tetranitro-9-fluorenylidenaminooxy)propionic acid[5] (TAPA) complexates more strongly with (−)-hexahelicene than with the (+) isomer[5] (in chloroform), but for compound IX the situation is reversed.[33] Preliminary experiments to resolve the heterohelicene IV with (+)-TAPA[34] showed that this compound behaves like IX and unlike hexahelicene. It seems a reasonable assumption that the complexating ability of (+)-TAPA with helicenes depends much more on the chirality than on minor structural features of the latter compounds, which leads to the same conclusion as made above.

As mentioned in the introductory statement, several other theories have been applied to correlate the optical activity and the absolute configuration of helically shaped molecules. Brewster,[4c] from classical wave theory of light and classical electromagnetics, predicted that right-handed helical molecule shows a positive optical rotation at long wavelength. Tinoco and Woody[4b] arrived at the same conclusion on the basis of free-electron theory. Both theories, although undoubtedly correct for properly selected compounds (for example, helically wound polyenes; *cf.* the model experiments with copper helices[31]), are in our opinion unsuited for helicenes, since the real structure of helicenes is much more complicated than that of the models used. MO calculations, on the other hand, suggest that the detailed structure and geometry of helicenes are very important. The optical rotation of hexahelicene VIII has also been calculated with the theory of Kirkwood.[4a] Again the right-handed enantiomer was calculated to show a positive optical rotation. Although these theories lead to the same assignment of the absolute configuration of the heterohelicenes which we concluded, they are in conflict with Moscowitz's assignment of the absolute configuration of hexahelicene (VIII). Our results do not unambiguously solve this long-standing problem, although the apparent utility of Moscowitz' method and the experimental evidence are strongly in favor of his assignment. Additional evidence emerges from the work of Weigang and coworkers.[14b,23] They pointed out that the detailed polarization of the transition giving rise to the β band in hexahelicene (as is the case for other helicenes) is quite simple and the transition truly involves displacement of electronic charge along the entire helical core of the molecule. The theories of Brewster[4c] and Tinoco and Woody[4b] should hold for such a transition and consequently the β band was predicted to show a positive circular dichroism for a P helicene.[14b] This prediction is in perfect agreement with our results, and the compound IX also seems to satisfy the rule.[6] In a subse-

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(29) R. A. W. Johnstone and S. D. Ward, *Tetrahedron*, **25**, 5485 (1969).

(30) The absolute value of $\langle\nabla_{cc}\rangle$ is not required for the calculations of the g values. One may, however, use the theoretical value of 4.1×10^7 cm^{-1} or the empirical value of 3.55×10^7 cm^{-1} (see ref 2 and 6).

(31) This follows from the fact that the transition $\psi_6 \rightarrow \psi_8$ has a lower energy than $\psi_7 \rightarrow \psi_9$.

(32) Configuration interaction, considering only $\psi_6 \rightarrow \psi_8$ and $\psi_7 \rightarrow \psi_9$, leads to a slightly increased (stronger negative) dichroism of the α band, and a slightly decreased dichroism of the β band. Whereas other configurations do not significantly contribute to the α band, the sign of which is thus definitely negative, they might influence to some extent the β band.

(33) M. S. Newman, R. G. Mentzer, and G. Slomp, *J. Amer. Chem. Soc.*, **85**, 4018 (1963).

(34) This observation was made by Mr. W. F. J. Huurdeman at this laboratory. The material obtained had a very low optical purity and no CD or ORD spectra of IV have been obtained thus far. These spectra, however, will most likely be quite similar to those of V.

quent paper,[23] (+)-hexahelicene was shown to exhibit a negative dichroism for the β band, which again suggests that the (−)-enantiomer must have the P configuration. It is interesting to note that the (+)-heterohelicenes, (−)-hexahelicene, and (+)-IX have also in common a very strong positive dichroism associated with the β' band. Since the origin of this band is uncertain and might differ for the various compounds, it is somewhat speculative to adopt this observation as a general rule. The investigation of more types of helicenes and heterohelicenes is needed to see whether such simple rules can be used safely for the correlation of their CD spectra. In addition, unambiguous proof of the absolute configuration of hexahelicene remains desirable.[35,36]

Experimental Section

Uv spectra (in cyclohexane solution) were measured with a Beckman DB-G spectrophotometer, ORD spectra (in chloroform solution) were determined with a Polarimatic 62 instrument, and CD spectra (in methanol solution) with a Roussel-Jouan Dichrographe II.

Table II. Uv Absorption Maxima (mμ) and Log ϵ Values[a]

Compd	
I	210 (4.54), 243 (4.75), 257 (4.41), 268 (4.37), 295 (3.80), 320 (4.20), 334 (4.29), 353 (3.63), 371 (3.76)
II	216 (4.75), 230 (4.67), 243 (4.65), 273 (4.47), 305 (3.94), 319 (3.90), 352 (4.22), 368 (4.27), 384 (3.98)
III	215 (4.62), 235 (4.60), 246 (4.50), sh 262 (4.48), 278 (4.28), 300 (3.85), 313 (3.82), sh 346 (4.21), 358 (4.26), 384 (3.95)
IV	227 (4.76), 253 (4.58), 277 (4.53), sh 317 (4.06), sh 324 (4.11), 329 (4.16), sh 355 (3.85), 372 (4.30), 391 (4.40)
V	218 (4.66), 229 (4.64), 277 (4.41), 316 (4.10), 330 (3.84), sh 356 (3.93), 371 (4.24), 391 (4.35)
VI	216 (4.72), 242 (4.64), sh 260 (4.47), 294 (4.27), 301 (4.22), 309 (4.22), 328 (3.87), sh 352 (4.03), 367 (4.28), 385 (4.30), sh 392 (4.23).
VII	215 (4.85), 225 (4.87), sh 250 (4.74), 359 (4.19), 376 (4.35), 412 (4.00), 435 (4.06).

[a] Cyclohexane solution, sh = shoulder.

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(35) I. Tinoco, Jr., and M. P. Freeman, *J. Phys. Chem.*, **61**, 1195 (1957).

(36) This is especially so since the results of recent calculations again do not favor Moscowitz's assignment (see footnote 9 of ref 1b).

Polar and Stereochemical Effects in the Addition of Triphenylaluminum to Para-Substituted Diphenylacetylenes[1,2]

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Abstract: To gain an understanding of the electronic factors governing the addition of the carbon–aluminum bond (carbalumination) to unsaturated hydrocarbons, the mechanism of the addition of triphenylaluminum to the triple bond of para-substituted diphenylacetylenes was investigated. The para substituents (Z) employed were the $(CH_3)_2N$, CH_3O, CH_3, CH_3S, H, Cl, CF_3, and CH_3SO_2 groups, but the acetylenes with the latter two substituents failed to react normally. The other acetylenes generally underwent stereospecific cis carbalumination to give a mixture of the two isomers, **6** and **7**, the logarithm of whose ratio correlated linearly with the Hammett σ values of the para substituent ($\rho = -0.713$) (see eq 2). The regioselectivity and cis stereospecificity, as well as the rate-retarding effect of donor solvents, are in accord with a kinetically controlled, electrophilic attack of the trivalent aluminum center on the triple bond, possibly with a bridging phenyl group diminishing the positive character on the acetylenic carbon.

The discovery of the ability of group IIIA metal alkyls and hydrides to add readily to unsaturated carbon–carbon bonds has transformed the whole field of hydrocarbon chemistry. Organoaluminum compounds have received particular attention during the past decade, both as stoichiometric reagents for forming new hydrocarbon skeletons[4] and as Ziegler–Natta catalyst components for the polymerization of olefins or acetylenes.[5] Despite the abundant progress in the synthetic applications of aluminum alkyls,[6] little is known about the stereochemistry, electronic factors, and kinetic details of the basic carbalumination reaction, that is, the addition of the carbon–aluminum bond to unsaturated carbon–carbon linkages.

The carbalumination of the acetylenic linkage appeared to be a most promising way of assessing both the polar and stereochemical factors determining the mode of addition of carbon–aluminum bonds to carbon–carbon unsaturation. Although the initial work of Wilke and Müller[7] with symmetrically substituted acet-

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(1) Part XVI of the series, "Organometallic Compounds of Group III," devoted to carbometallation and hydrometallation of unsaturated carbon–carbon bonds.

(2) Previous related parts: *J. Organometal. Chem.*, **21**, 21, 285 (1970); **16**, P55 (1969); **12**, P33 (1968); **11**, P7, P50 (1968); **8**, 53 (1967); *ibid.*, **4**, 415 (1965); **2**, 184 (1967); *J. Amer. Chem. Soc.*, **88**, 2213, 2976 (1966); **86**, 4221 (1964); **84**, 3605, 3830 (1962); *J. Org. Chem.*, **31**, 3419 (1966).

(3) National Aeronautics and Space Administration Trainee, 1963–1966.

(4) K. Ziegler, *et al.*, *Justus Liebigs Ann. Chem.*, **629**, 1 (1960); H. Lehmkuhl, K. Ziegler, and H.-G. Gellert, in "Houben-Weyl Methoden der organischen Chemie," Vol. XIII/4, E. Müller, Ed., Thieme Verlag, Stuttgart, 1970.

(5) *Cf.* the excellent review by J. P. Kennedy and A. W. Langer, Jr., *Fortschr. Hochpolym.-Forsch.*, **3**, 508 (1964).

(6) *Cf.* the excellent review by G. Bruno, "The Use of Aluminum Alkyls in Organic Synthesis," Ethyl Corporation, Baton Rouge, La., 1970, p 75, with 473 references.