Table II. Selected Ions from the Flash Vaporization Mass Spectrum of the Product Mixture from the Reaction of Lithium Vapor and CCl_4

positive ion	*m*/*e*	positive ion	*m*/*e*
CLi	19	C_2Li_8	80
CLi_2	26	C_3Li_{11}	113
CLi_3	33	C_3L_{12}	120
CLi_4	40	C_3Li_3	69
CLi_5	47	C_4Li_4	76
C_2Li	31	C_6Li_5	107
C_2Li_2	38	C_6Li_6	114
C_2Li_7	73		

indicated to be nearly electroneutral at this level. Absolute energies of **3** along with those of the species used in eq 1–7 are given in Table I.

By imposition of C_{4v} symmetry, an additional CLi_5^+ isomer, **3′**, could be calculated. The unique C–Li_a bond distance is 1.959 (1.998) Å at STO-3G(3-21G); C–Li_b = 1.965 (2.012 Å) and Li_aCLi_b = 101.5° (101.2°). The energies of **3′** (C_{4v}) are only 1.0 (0.8) kcal/mol, STO-3G(3-21G), above those of **3** (D_{3h}). Hence, the energy surface of CLi_5^+ should be extremely flat, with almost no activation required for scrambling (pseudorotation).

The large exothermicity of eq 1 and 2 indicates the stability

	energies, kcal/mol				
	STO-3G	3-21G	4-31G	exptl	
$CLi_4 + Li^+ \rightarrow CLi_5^+$	−85.4	−85.2	−83.6	–	(1)
$CLi_3^+ + Li_2 \rightarrow CLi_5^+$	−77.6	−62.2	−60.9	–	(2)
$CH_4 + H^+ \rightarrow CH_5^+$	−120.5	−115.3	−117.6	−127[11]	(3)
$CH_3^+ + H_2 \rightarrow CH_5^+$	−13.7	−17.9	−15.8	−40[11]	(4)

of CLi_5^+ toward the most likely modes of dissociation. The enormous stabilization of both carbonium ions[1] and carbenium ions[12] by Li substitution has been noted earlier. Both CLi_3^+ and, possibly, CLi_4^+ have been reported experimentally.[13] These ions, CLi_5^+, and many other lithiated carbocations are found in the present study (Table II). Even though the H^+ affinity of CH_4 (eq 3) is considerably higher than the Li^+ affinity of CLi_4 (eq 1), CH_5^+ has a more favorable decomposition pathway (eq 4) compared to CLi_5^+ (eq 2). Since the basis sets employed here underestimate the stability of CH_5^+, errors in CLi_5^+ are likely to be in the same direction. The theoretical prediction that CLi_5^+ should be very stable thermodynamically has now been confirmed experimentally.

Tetralithiomethane, $(CLi_4)_n$, was prepared by the Lagow procedure by reacting lithium vapor with carbon tetrachloride.[14] A sample of the solid $(CLi_4)_n$, which must be handled under argon, was then studied with a specially designed flash vaporization mass spectrometric probe, capable of nonequilibrium vaporization of the sample at 1500 °C.[15] A selection of peaks observed mass spectrally are given in Table II. The elemental composition of CLi_5^+ (47.0800 amu) was established by exact mass measurements. Besides the observation of CLi_5^+ for the first time, the results establish that CLi_4 was produced;[14] its dimer, C_2Li_8, and trimer, C_3Li_{12}, are also indicated to be present. CLi_3^+ and its CLi_4 complex, $C_2Li_7^+$, also are found, as are $(C_2Li_2)_n^+$ (n = 1–3) and corresponding ions in which one lithium atom has been lost.

We considered CLi_6^{2+} next. Would the stabilizing influence of the six lithiums overcome the electrostatic repulsion inherent in dications? We probed only the most likely octahedral symmetry, **4**. The optimized C–Li distances were 2.063 Å at STO-3G, 2.094 Å at 3-21G, and 2.090 Å at 4-31G. Like **3**, the STO-3G charges, C = −0.05 and Li = 0.34, indicate CLi_6^{2+} to have an essentially neutral central carbon bonded to a "sphere" of partially positively charged lithium atoms. The stability toward decompositions was examined by using reactions 5–7. Equations 5 and

	energies, kcal/mol			
	STO-3G	3-21G	4-31G	
$CLi_4 + 2Li^+ \rightarrow CLi_6^{2+}$	−72.6	−78.2	−74.7	(5)
$CLi_3^+ + Li_3^+ \rightarrow CLi_6^{2+}$	−12.0	−12.9	−8.5	(6)
$CLi_5^+ + Li^+ \rightarrow CLi_6^{2+}$	+12.8	+7.0	+8.9	(7)

6 are exothermic. The only favorable decomposition mode is indicated by eq 7 which, as written, is somewhat endothermic; however, this may change at higher theoretical levels.

Further calculations not feasible at present will be needed before the existence of CLi_6^{2+} can be predicted theoretically. However, the STO-3G//STO-3G frequencies indicate octahedral CLi_6^{2+} to be a local minimum; thus, eq 7 should be associated with a kinetic barrier. The electronic structures of these high-symmetry systems, CLi_5^+ and CLi_6^{2+}, follow the general pattern of D_{3h} and O_h molecular orbitals discussed by Gimarc.[10] Since only octets of valence electrons are present, these ions are hypercoordinate but not hypervalent. However, the present results also imply the existence of neutral hypervalent carbon–lithium compounds, e.g., CLi_5 and C_2Li_8. In addition to these species, our calculations (to be reported subsequently) indicate CLi_6^+, CLi_6, and CLi_8 to be stable thermodynamically.[16]

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Registry No. H_2, 1333-74-0; Li^+, 17341-24-1; Li_2, 14452-59-6; Li_3^+, 12596-48-4; CH_3^+, 14531-53-4; CLi_3^+, 81506-46-9; CH_4, 74-82-8; CH_5^+, 15135-49-6; CLi_4, 38827-79-1; CLi_5^+, 81616-33-3; CLi_6^{2+}, 81616-34-4.

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Inherently Dissymmetric Chromophores and Vibrational Circular Dichroism. The CH_2–CH_2–C*H Fragment

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The concept of the "inherently dissymmetric chromophore"[1] has proved quite useful for the stereochemical interpretation of circular dichroism (CD) spectra of electronic origin.[2] In the present communication we point out that the same concept can be used to marked advantage in the case of vibrational circular dichroism (VCD) spectra.[3,4] We illustrate the point by way of the inherently dissymmetric CH_2–CH_2–C*H fragment ubiquitous in six-membered ring compounds that approximate the chair conformation.

An inherently dissymmetric chromophore is one whose local (inherent) symmetry is sufficiently low that, even in isolation, its associated transitions are both electric and magnetic dipole allowed

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Table I. Observed Frequencies and Sign Patterns for the Characteristic VCD Bands of the CH_2–CH_2–C*H Fragments in Molecules of Known Absolute Configuration

molecule	observed band maxima, ±3 cm^{-1}	observed sign pattern	predicted sign pattern
(*R*)-(+)-3-methylcyclohexanone	2948, 2929, 2912	+–+	+–+
(*R*)-(+)-3-methylcyclohexanone-*2,2,6,6-d*$_4$	2951, 2930, 2915	+–+	+–+
(*R*)-(+)-3-*tert*-butylcyclohexanone	2953, 2934, 2913	+–+	+–+
(*R*)-(+)-3-*tert*-butylcyclohexanone-*2,2,6,6-d*$_4$	2953, 2934, 2915	+–+	+–+
(–)-menthone	2948, 2928, 2909	+–+	+–+
(+)-isomenthone	2954, 2935, 2906	–+–	–+–
(+)-limonene	2939, 2915, 2893	+–+	+–+
(+)-*p*-menth-1-ene	2942, 2925, 2895	+–+	+–+
(+)-*p*-menth-1-en-9-ol	2960, 2923, 2893	+–+	+–+
(–)-*β*-pinene	2956, 2939, 2922	–+–	–+–
(–)-*α*-pinene	pattern absent	pattern absent	
(–)-*cis*-myrtanylamine	2970, 2944, 2923	+–+	+–+
(+)-pulegone	2949, 2927, 2903	+–+	+–+
(–)-menthol	2945, 2928, 2911	+–+	+–+
(–)-perillyl alcohol	2941, 2921, 2892	–+–	–+–

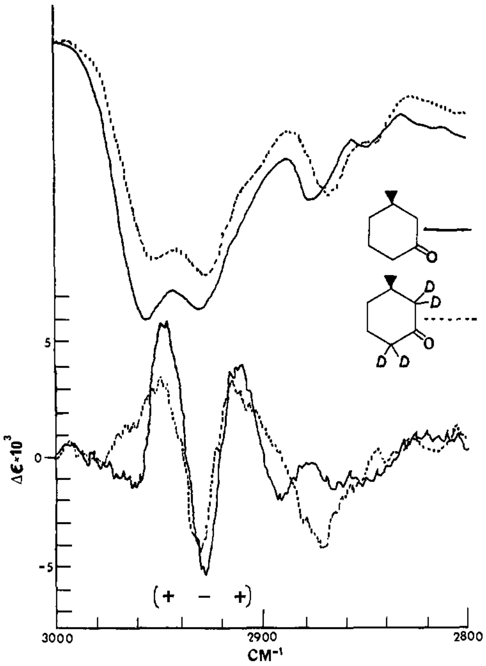

Figure 1. VCD (lower traces) and transmission spectra (upper traces) between 3000 and 2800 cm^{-1} of (*R*)-(+)-3-methylcyclohexanone (—), 0.048 M in CCl_4, and its *2,2,6,6-d*$_4$ derivative (---), 0.045 M in CCl_4.

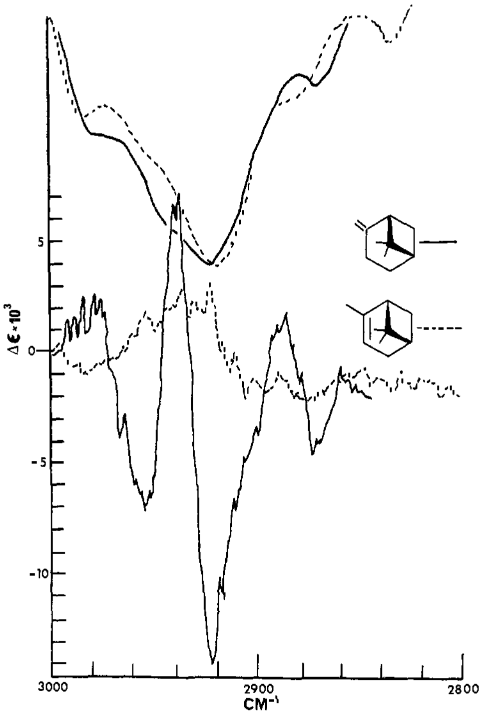

Figure 2. VCD (lower traces) and transmission spectra (upper traces) between 3000 and 2800 cm^{-1} of (–)-*β*-pinene (—), 0.049 M in CCl_4, and (–)-*α*-pinene (---), 0.049 M in CCl_4.

and hence can exhibit relatively large CD bands. Consequently, when such chromophores are incorporated into a molecule, the signed intensities of the molecular CD bands attributable to the chromophore are dominantly a reflection of the absolute chiral geometry of the chromophoric fragment. In these instances, one can pose and answer problems of stereochemistry whose solutions follow from a knowledge of the absolute geometry of the chromophoric fragment. And this latter information is forthcoming from the measured signs of the relevant CD bands.

In Figure 1 we show the transmission and VCD spectra in the CH stretching region of (*R*)-(+)-3-methylcyclohexanone and its *2,2,6,6-d*$_4$ derivative. Comparison of the VCD spectra of the deuterated and undeuterated species strongly indicates that the (+–+) pattern created by the bands at about 2950, 2930, and 2910 cm^{-1} is to be associated with three of the possible stretching modes of the CH_2–CH_2–C*H fragment of the ring. A similar pattern, but of opposite sign, i.e., (–+–), appears in the VCD spectrum of (–)-*β*-pinene but not in that of (–)-*α*-pinene (Figure 2). Note that *β*-pinene contains the relevant fragment; *α*-pinene does not. Further, in Table I we list a number of six-membered ring compounds of well-known absolute configuration belonging to a variety of chemical classes, e.g., alcohols, terpenes, etc. All of these compounds contain the CH_2–CH_2–C*H moiety, and all exhibit a (+–+) or a (–+–) pattern of VCD bands in the pertinent CH stretching region.

On the basis of previous assignments made for CH stretching modes in such molecules[5,6] and also on the basis of a normal coordinate analysis we have performed for the fragment,[7] we assign the three observed bands to the three modes generated by a coupling among the two locally antisymmetric methylene stretching modes and the C*H stretching mode of the CH_2–CH_2–C*H fragment. On both empirical grounds and a theoretical calculation of the signed rotational strengths of the pertinent normal modes,[7] we assign the (+–+) pattern and the (–+–) pattern, respectively, to the absolute configuration of the CH_2–CH_2–C*H fragment in the two possible chair conformations indicated in Figure 3. These two dissymmetric CH_2–CH_2–C*H geometries are not truly enantiomeric because of the differences

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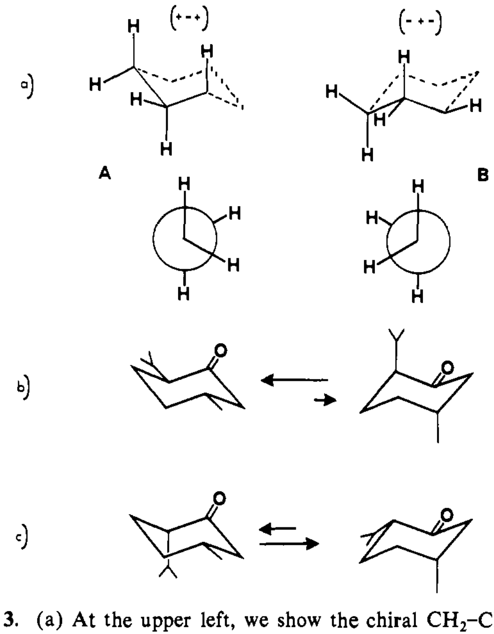

Figure 3. (a) At the upper left, we show the chiral CH_2–CH_2–C*H geometry A that gives rise to a (+−+) sign pattern in the pertinent CH stretching region; at the upper right, we show the chiral CH_2–CH_2–C*H geometry B that gives rise to a (−+−) sign pattern. We show also the Newman projections of the two methylene groups in the CH_2–CH_2–C*H fragments for geometry A and geometry B: (b) chair equilibrium in (−)-menthone; (c) chair equilibrium in (+)-isomethone.

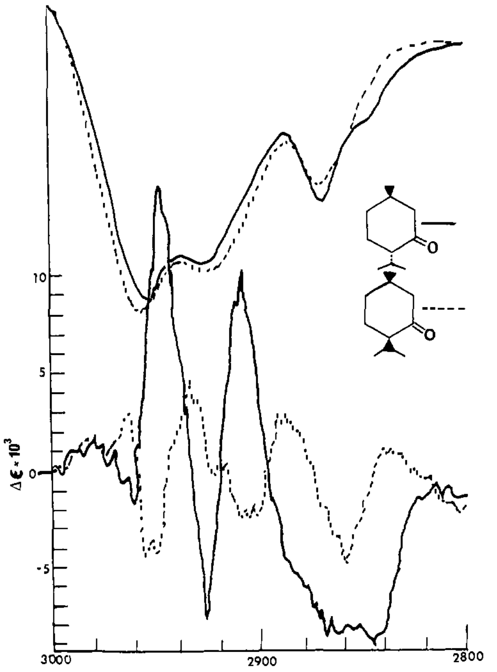

Figure 4. VCD (lower traces) and transmission spectra (upper traces) between 3000 and 2800 cm^{-1} of (−)-menthone (—), 0.059 M in CCl_4, and (+)-isomenthone (- - -), 0.062 M in CCl_4.

in the disposition of the methine CH bond relative to the methylene CH bonds in the two instances. Nevertheless, on both empirical and computational grounds,[7] the deviations from a strict mirror-image geometrical relationship are not sufficient to spoil the enantiomeric-like relationship between the two sign patterns, i.e., (+−+) for geometry A vs. (−+−) for geometry B.

In Table I we also give the patterns predicted on the basis of the known absolute configuration of the compounds listed. In cases where there would be significant conformational mobility, prior knowledge of the absolute configuration allows one to assign the dominant conformer. This is the situation for (−)-menthone and (+)-isomenthone, whose oppositely signed VCD spectral patterns, shown in Figure 4, are indicative of the dominant conformers indicated in Figure 3b,c.

We have not yet encountered any exceptions to the stated correlation of VCD sign patterns with the chiral sense of the CH_2–CH_2–C*H fragment. Nevertheless, we do call attention to a caveat that carriers over, mutatis mutandis, from the analogous stereochemical analysis of electronic CD data: the isolated nature of the chromophoric transitions must not be destroyed through coupling with other vibrational modes or through the accidental overlapping of the relevant chromophoric CD pattern by other CD bands.[8]

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Registry No. (*R*)-(+)-3-Methylcyclohexanone, 13368-65-5; (*R*)-(+)-3-methylcyclohexanone-2,2,6,6-d_4, 82209-32-3; (*R*)-(+)-3-*tert*-butylcyclohexanone, 72029-73-3; (*R*)-3-*tert*-butylcyclohexanone-2,2,6,6-d_4, 82209-33-4; (−)-menthone, 14073-97-3; (+)-isomenthone, 18309-28-9; (+)-limonene, 5989-27-5; (+)-*p*-menth-1-ene, 1195-31-9; (+)-*p*-menth-1-en-9-ol, 13835-75-1; (−)-β-pinene, 18172-67-3; (−)-*cis*-myrtanylamine, 73522-42-6; (+)-pulegone, 89-82-7; (−)-menthol, 2216-51-5; (−)-perillyl alcohol, 18457-55-1.

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Transition-Metal-Promoted Carbon–Carbon Bond Formation by Reductive Dimerization of Carbon Disulfide: Direct Synthesis of the Bis(1,2-dithiolene-like) Tetrathiooxalato (C_2S_4) Ligand from Carbon Disulfide by Reaction with the Dimeric Nickel(I) Complexes $Ni_2(\eta^5\text{-}C_5R_5)_2(\mu\text{-}CO)_2$ (R = H, Me)

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Although intensive efforts have been devoted during recent years to prepare and characterize metal-bound CO_2 complexes in conjunction with CO_2 fixation via reactions with transition-metal systems,[2] only a few metal-coordinated CO_2 complexes have been isolated and crystallographically ascertained.[3-6] These include a novel d^6 Ir(III) $IrCl(C_2O_4)(PMe_3)_3$ product[6] in which the C_2O_4 ligand has been formed from a *head-to-tail* O_2C–OCO dimerization of CO_2 by initial reaction with a d^8 Ir(I) complex. On the other hand, the more reactive, related cumulene (or heteroallene) carbon disulfide has been shown from structural studies[2,7,8] to

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