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OPTICAL ACTIVITY OF SOME HYDROCARBONS

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Just 100 years ago Jacobus van't Hoff[1] transformed organic chemistry from a 2-dimensional to a 3-dimensional science. In proposing the tetrahedral structure for the bonding pattern around a saturated C atom Van't Hoff, with one stroke, provided new insight into the chemical and physical properties of most organic compounds.

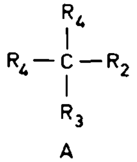
In this paper we would like to examine some of the relations between optical activity and the tetrahedral structure.

Van't Hoff gave a new dimension to our understanding of organic chemistry by examining the consequences of going from a planar to a tetrahedral carbon. We have looked at the consequences of flattening a tetrahedrally substituted carbon structure and of bending a planar π bonded structure.

I. An asymmetric alkane.
II. A dissymmetric spiro[3.3]heptane and
III. A symmetric aromatic ring.

CASE I. THE CASE OF ASYMMETRIC HYDROCARBON WHICH REFUSED TO ROTATE THE PLANE OF POLARIZED LIGHT

The starting point of most of Van't Hoff's ideas is symbolized by the structure A below.

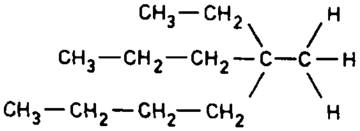


A

As classically stated, an organic compound is asymmetric, and as a consequence it will rotate the plane of polarized light, if (and only if) $R_1 \neq R_2 \neq R_3 \neq R_4$.

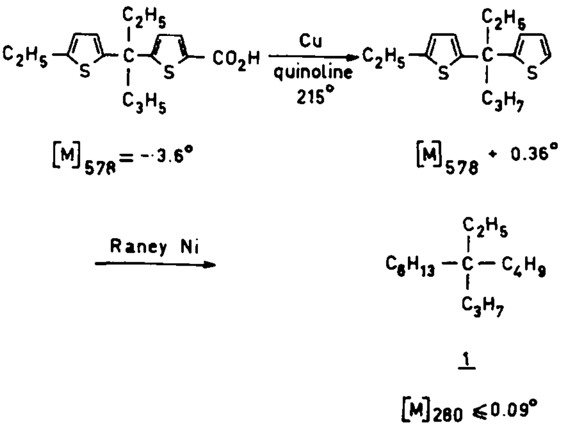
What are the measurable limits if R_1 is different from R_2? We defined the problem for the simplest case as follows: if R_1, R_2, R_3 and R_4 were alkyl groups in structure A, would the difference in the length of the alkyl chain be sufficient to impart measurable optical activity on A and thus fall within Van't Hoff's definition of $R_1 \neq R_2 \neq R_3 \neq R_4$?

We set out to prepare one enantiomer of the hydrocarbon 1, namely butylethylhexylpropylmethane. An important consideration in the choice of this hydrocarbon is the absence of a methyl group, $R_1 = -CH_3$, as one of the side chains. Since, as we will note later again, polarizability plays an important part in determining the magnitude of optical activity, it was necessary to minimize differences in polarizability, while retaining differences in the length of the alkyl chain. However, when a methyl group is attached to a chiral carbon center as in structure B this group contributes differently to the polarizability than the remaining alkyl chains.[3] The one extra C–H bond in the methyl group, *close to the* chiral carbon center, causes this polarizability difference. The three other carbons surrounding the chiral carbon are identical in this respect.



B

The synthesis was designed in such a manner that it could be proven without doubt† that the end product 1 consisted of one enantiomer. The last steps in the synthesis are shown in Scheme 1.[2]



SCHEME 1.

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†The original paper[2] should be consulted for the proof of structure of hydrocarbon 1, and its purity.

Attempts were made to measure the rotation of the asymmetric hydrocarbon 1 in a number of ways. The hydrocarbon was purified to such an extent that measurements of the rotations of the neat liquid were possible. Measurements were carried out at various temperatures and with different instruments. Both enantiomers were prepared, and attempts were made to maximize the scale deflections by comparing the two enantiomers directly. Enantiomerically pure hydrocarbon 1 showed no rotation above 280 nm with present day instruments.

Two explanations for this experimental fact may be proposed.

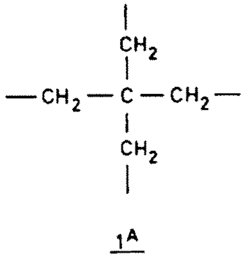
I. *The first, or "acceptable" explanation for the lack of optical activity in enantiomerically pure* 1:

The optical activity of an asymmetric compound is caused by absorption (loss of light energy) and dispersion (decrease of the velocity of light) effects.

a. *Absorption effects*

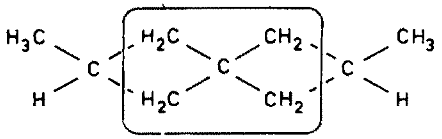
Hydrocarbon 1 has only σ-σ^* transitions and must then be a "chromophore" below 200 nm. This chromophore is either symmetric or asymmetric depending on the way we want to look at it. It is symmetric if we only consider the following molecular grouping (1A), but inherently asymmetric when the entire molecule and thus all of the σ-σ^* transitions are taken into account. In this respect the similarity to dimethylspiro[3.3]heptane (2) is striking. Case II will examine the latter molecule in detail.

At any rate, based on a σ-σ^* absorption argument only, we might expect a Cotton effect in the far UV region for 1. If, in addition, dispersion factors are small (or averaged out), the rotation will decrease steadily from the vacuum UV to the visible region.



$$-CH_2-\underset{\underset{|}{CH_2}}{\overset{\overset{|}{CH_2}}{C}}-CH_2-$$

1A



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b. *Dispersion effects*

There are three separate but related dispersion factors which contribute to the vanishing optical activity.

1. The differences in polarizability of the four alkyl chains[3,4] are small.

2. Whatever differences exist, the effects are further dampened by the four -identical- CH_2 groups surrounding the chirally substituted C atom.

3. The net conformational asymmetry contribution is zero or vanishingly small. Using Brewster's classical paper[5] as guide, low energy conformations can be drawn for each of the four alkyl chains. A total of 459 conformations are found in this manner.[6] The summation of the contribution to the conformational asymmetry of these 459 conformations is zero. The conformations of the bondings attached to the asymmetric atom show (necessarily) the forbidden double skew pattern.[5,6]

Conclusion

The combination of minute perturbation and σ-σ^* transition thus leads to non-observable rotation in the region > 280 nm.[2] Careful ORD measurements below 250 nm might well reveal a small rotation. We do not expect significant temperature effects.

II. *Perhaps hydrocarbon* 1 *has become racemized*!

The second, seemingly unlikely explanation for the lack of optical activity in enantiomerically pure 1 is that the hydrocarbon has become racemic. Two modes of racemization namely a dissociation mechanism or an inversion mechanism may be advanced.

(a) *The dissociation mechanism.* Dissociation of hydrocarbon 1 into fragments may occur during or after the desulphurization step. Crucial is the breaking of a bond attached to the chiral carbon atom regardless of the nature (radical or ionic) of the short-lived intermediate. A dissociation mechanism as shown in Scheme 2 would cause racemization! Recombination to the original compound would not however proceed in high yield if at all. The mass spectrum of analytically pure 1 shows the loss of fragments C_2H_5, C_3H_7, C_4H_9 and C_6H_{13} only.

(b) *An inversion mechanism.* We are left with the most unlikely explanation possible in light of Van't Hoff's tetrahedral postulate. Hydrocarbon 1 has racemized by assuming—at some time during its conversion from the thiophene precursor—a planar and therefore a symmetrical structure.†

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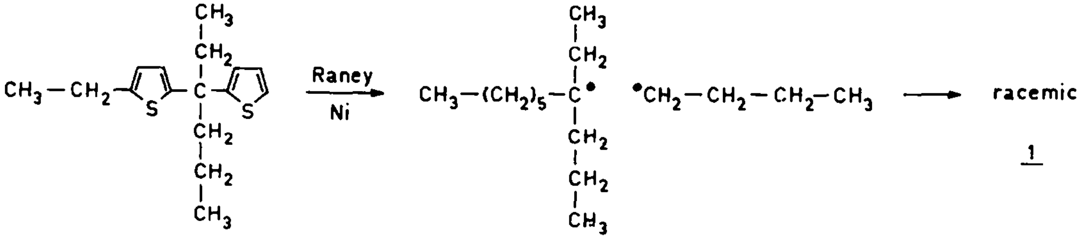
†Another concept for racemization has been suggested by L. Salem, *J. Am. Chem. Soc.* **95**, 94 (1973).



Scheme 2.

Table 1. Energy of planar methane[a]

	ΔE (kcal/mole)		ΔE (kcal/mole)		ΔE (kcal/mole)
method 1[b]	248	method 4[d]	168	method 7[f]	35–40
method 2[c]	127	method 5[e]	250		
method 3[c]	187	method 6[e]	180		

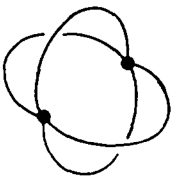
[a] Values of energy above that of planar methane, [b] Ref 7, [c] Ref 8, [d] Ref 9, [e] Ref 10, [f] Ref 11.

In order to simplify and at the same time generalize the problem let us state the question as follows: under what conditions—of energy and structure—can the four substituents covalently bonded to a C atom lie in a plane with this C atom? We have asked a number of colleagues this question and Table 1 gives a summary of the answers to date.

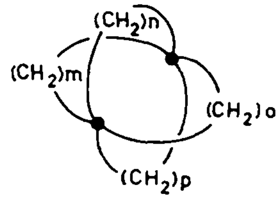
Intriguing is the vast spread in strain energy values assigned to a "planar carbon" structure. It certainly behooves the theoretical chemists to get together and let us know whom (or what) to believe...

We have also made several attempts to approach the problem experimentally. Instead of trying to prepare one compound with "planar carbon", we have tried to approach a planar carbon structure via a reversible reaction. Scheme 3 embodies the idea. Structure 4, a "paddlane"[12] formally belongs to a class of compounds, whose generalized structure is 5 and 6.

It is evident that the C atoms at the bridge of 5 and 6 will have an increasing "planar" surrounding as the number of atoms (m, n, o, p) in the bridges decreases.



5



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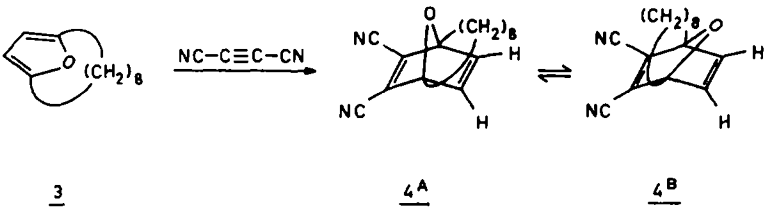
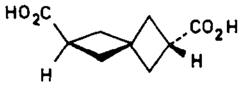
If, as in the case in the Diels–Alder addition to the furanophane 3, the reaction is reversible, then it should be possible to establish (one) energetic limit on (one) "planar carbon" molecule by shortening the hydrocarbon bridge. Thus, if instead of eight methylene groups in 3 the furanophane with a smaller number of methylene groups fails to undergo the Diels–Alder addition to furnish a stable "paddlane", one explanation of this failure may be in the strain around the bridge C atoms.

CASE II. THE CASE OF THE STUBBORN SPIRANE

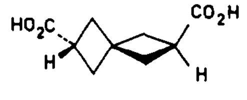
Some years ago[13] we made an attempt to establish the absolute configuration of Fecht acid or spiro [3.3]heptane - 2,6 - dicarboxylic acid (7). At that time (1971) we assigned the *R* configuration to dextrorotatory Fecht acid (7A).



Scheme 3.



7A



7B

Van't Hoff[1] predicted that properly substituted allenes and in consequence also spiranes could be resolved. In particular, for spiranes the capability of resolution was recognized by Aschan in 1902.[14] Since then, the resolvability has been amply verified.[15,16]

As with all compounds whose dissymmetry depends on the entire molecular structure and not on one or more chiral centers, determination of the absolute configuration by the usual correlation methods poses special problems. For a carbocyclic spirane (spiro[4.4]nonane) case for example it was not until 1968 that Gerlach[17] succeeded in assigning the absolute configuration. Using the method of Horeau, his assignment is based on the stereochemistry of the related spiro[4.4]nonane - 1,6 - diol and is inapplicable to the spiro[3.3]heptane case. The corresponding 1,5 diols are presently inaccessible.*

Table 2. Configurational assignment to Fecht acid 7

Method	Assignment
1. Application of Lowe's rule[a]	R-(+)-7
2. Application of Klyne's sector rule[b]	R-(+)-7
3. Brewster's uniform conductor model[c]	R-(+)-7
4. Kirkwood's polarizability model[d]	R-(+)-7
5. Eyring-Jones' model[e]	R-(+)-7
6. Anomalous X-ray scattering analysis of the (free) Fecht acid by filmdata[f]	R-(+)-7
Idem by diffractometer data[g]	S-(+)-7
7. Idem for a barium salt of 7[g,h]	S-(+)-7

[a] Ref 13; Lowe's rule in Ref 20

[b] Refs 19*a* and 21

[c] Ref 4

[d] Refs 4 and 22

[e] Refs 4 and 23, this model was applied to 3

[f] 75% of the cases checked pointed to this assignment, see Ref 19*a*

[g] Ref 19*c*; 88% of the cases checked pointed to this assignment

[h] Both 100% of all cases checked on films and *R* index comparison method for the *S* and *R* configurations pointed to this assignment

Recently, we reexamined the assignment, R-(+)-7, critically.[19] The following techniques were applied (Table 2).

As can be seen from the above data 5 apparently independent empirical and theoretical techniques furnished the same result (*R* configuration for dextrorotatory Fecht acid), while only the 7th technique led to a clearly contrary result.

We have come to the conclusion that the last assignment, namely the *S* configuration (**7B**) for dextrorotatory Fecht acid is correct. We wish to examine in some detail the reasons for the failure of the first technique to furnish the correct answer. The successive 4 techniques will be discussed briefly.

The failure of the (five) theoretical, empirical or semi-empirical models (Nos. 1, 2, 3, 4 and 5 in Table 2) of optical activity to predict correctly the absolute configuration should not be interpreted in a negative manner. We feel that this failure implies nothing concerning the original Bijvoet work[24] as had been suggested in a triptycene case by Tanaka.[25] Recent calculations[26] and experiments[27] amply reconfirm the correctness of Bijvoet's original postulates. The failure of the empirical and theoretical models is valuable as a negative result and actually reveals hitherto hidden structural differences between classes of compounds.

A. *Lowe's rule*

Most if not all textbooks on stereochemistry treat the subject of allenes and spiranes in one section. This is unfortunate but not surprising since the symmetry properties of allenes and spiranes are the same for a number of cases. That is allenes (type A in Fig 1) and spiranes of type B (Fig 1) have C_1 or C_2 symmetry.

A B

Fig 1.

Lowe's rule,[20] subsequently developed by Brewster,[4] relates the absolute configuration of a chiral allene to the sign of its rotation at the sodium D-line on the basis of the screw pattern of polarizability of the substituents. This rule ignores bonding and conformation effects. When applied to allenes as Lowe's rule initially was meant to be, this led to internally consistent results.† In properly substi-

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*Oxidation and subsequent reduction of the known 1,5-dimethylene spiro[3.3]heptane[18] might give valuable information for potential solution of the problem for 1,5-disubstituted spiro[3.3]heptanes.

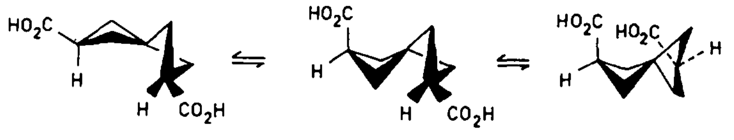
†There is only one exception known in the literature to Lowe's rule as applied to allenes (cyclonona - 1,2 - diene).[29] In this compound the methylene bridge is present in one of both hemispheres of the skeleton leading to sign reversal for the lowest-energy Cotton effect.

tuted allenes[28] the 1,2-diene skeleton as the chiral chromophore can be expected to dominate virtually all absorption and dispersion effects which jointly cause the Cotton effects.

Although in allenes substituted with carboxyl groups weak n-π^* electronic transitions can and do lead to strong Cotton effects, these apparently do *not* dominate the sign at long wavelengths (sodium D line). Either conformational rigidity in the direct vicinity of the carboxyl chromophore (as in steroids) or highly polarizable substituents (increasing the dissymmetric perturbation) would be needed before these transitions would dominate the influence originated from the allene skeleton. It seems to us that this is the major reason that Lowe's rule is internally consistent for allenes.† Finally it is necessary to point out that *any rule which correlates absolute configuration to the optical activity at a single wavelength, is open to criticism.* We suggest that the extent to which a chiroptical rule (Lowe's rule,[20] as well as the theoretical models of optical activity[4,22] are chiroptical rules)—is valid increases, the closer, the wavelength at which the rotation is measured approaches the λ_{max} of that Cotton effect which reflects the most significant dissymmetric portion of the molecule.‡ The restrictions on a generally valid chiroptical rule are obviously many. Since many stereochemists make use of rules based on empiricism and theory for assigning an absolute configuration, our experience with the failure of Lowe's rule is worthy of study.

If we therefore ignore bonding and conformation as an important factor in establishing a relationship between the sign of rotation and the absolute configuration it is clear that this relationship (Lowe's rule) must fail when either bonding or conformation or both become important.

The structure of Fecht acid 7 as demonstrated by the X-ray analysis for the solid phase[19a] and by NMR analysis for some related spiranes in solution[30] reveals that this compound is best represented—in solution and at room temperature—as in Fig 2.

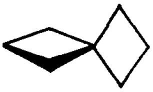


e,e a,e a,a

Fig 2.

The following features are of importance:

1. Conformer e,e (Fig 2) is present in concentrations approaching 100% in solution.
2. The 4-membered rings are puckered instead of flat.
3. The puckered ring is subject to conformational mobility.
4. The angles and bond lengths of the spirane skeleton show real and significant differences, especially around the spiro atom. Spiro[3.3]heptanes do not, therefore, resemble the pretty symmetrical drawing C:



C

5. Substituents on the 2,6-positions of the spiro[3.3]heptane skeleton have conformational preference and mobility.

The consequences of these structural features are the following.

1. The hydrocarbon portion of the molecule, that is the spiro[3.3]heptane skeleton, has a dissymmetric conformation. This dissymmetry is superimposed upon the dissymmetry resulting from 2,6-disubstitution.
2. The 2,6-substituents themselves add further dissymmetry to the entire molecule due to preferred, asymmetric conformations.

These *three* separate but interrelated dissymmetry elements contribute differently to the optical activity.

(a) The spirane skeleton, a strained, somewhat mobile saturated hydrocarbon is not expected to show large rotations between 232 nm and 578 nm (see case I).§ This is borne out by experimental results. Thus *l*-2,6-dimethylspiro[3.3]heptane shows a molecular rotation $[M]^{20}_{578}$ $-5{\cdot}8°$ (*c* 1·8, cyclohexane) which slowly increases to $-16{\cdot}6°$ at

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†There is only one exception known in the literature to Lowe's rule as applied to allenes (cyclonona-1,2-diene).[29] In this compound the methylene bridge is present in one of both hemispheres of the skeleton leading to sign reversal for the lowest-energy Cotton effect.

‡In addition, it is necessary that the sign of the pure rotational strength of that transition is not influenced by conformational mobility, solvatation and special asymmetric orientations of the substituents attached to that portion of the molecule.

§Attempts to prepare optically pure 2,6-di-t-butyl-2,6-dimethyl spiro[3.3]heptane are in progress. This compound may reveal the contribution of the bare skeleton to the optical activity.

365 nm.[13] Any Cotton effects are expected to manifest themselves far below 200 nm due to the short wavelength σ-σ^* transitions and the absence of other transitions.

(b) The presence of a carboxyl functionality (or any functionality containing a chromophore with π-π^* or n-π^* transitions) can and does mask the influence of the σ-σ^* transition in the 200–600 nm region. This means that the sign of rotation for 7 at long wavelengths (sodium D-line) may well be due to the Cotton effect for the n-π^* transition of the carboxyl group, and that this sign bears no relation to the dissymmetry of the spirane skeleton itself. This turned out to be the case. Sign reversal is observed when the carboxyl n-π^* transition is removed (conversion to 3, Fig 3)[13] or quenched (sulfuric acid, Table 3 and Fig 4).[31]

B. *Klyne's sector rule and theoretical models of optical activity*

Klyne's sector rule for carboxylic acids[21] does not hold in our spirane case either. Referring to the previous rule it is not surprising that an empirical rule is not reliable in general when applied to different classes of compounds without other classical X-ray confirmatory evidence. It should be stressed in this regard that the conformational situation of 7 in the solid phase does not differ greatly from that in solution.

The reasons for the failing of the major models of optical activity[19c,31] is to be found in the limitations imposed by the overriding need for simplicity and by the fact that these models rest upon a number of arguments by analogy.[4] They do not take into account in their crude approximation all possible contributions to the optical activity in the longer wavelength region.

The low optical activity of our spiranes fortuitously revealed the discrepancy of these models and also the anti-Lowe and anti-Klyne behaviour of Fecht acid and its large series of derivatives.

CASE III. FLEXIBLE PLANAR MOLECULES

The previous two cases have shown us that worthwhile new insight into the properties of simple organic compounds can be obtained by questioning the postulate of Van't Hoff, saturated carbon compounds are tetrahedrally oriented in space. However, a reverse situation prevails with unsaturated compounds. Planar Hückel aromatic compounds, planar benzene or naphthalene have assumed such a solid place in our thinking and vocabulary that only very recently[32] the question has been raised: "what does it take to bend a benzene ring?"

Experimental work by Brown,[33] Allinger,[41] Cram,[34] Schmidt,[35], Newman,[36] Martin,[37] Lawton[38] and in our laboratory[39] was a sufficient basis to propose the concept of flexible aromatic rings. Table 4 summarizes our initial results with this concept. It appears that—at least to a 15–20° extent, mono- but

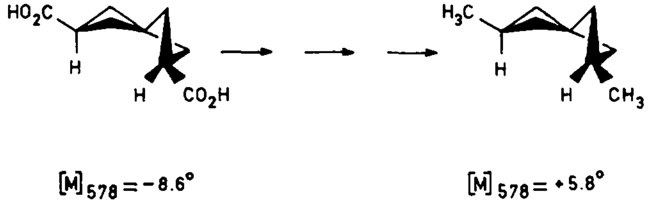


Fig 3.

Table 3. Special solvent affects of d-7

Solvent	$[M]_{578}$	$[M]_{546}$	$[M]_{436}$	$[M]_{405}$	$[M]_{365}$	Concentration
Acetone	+1·8°	+2·6°	+5·2°	+6·3°	+8·8°	5·0
2N H_2SO_4	+0·7°	+1·3°	+2·6°	+4·0°	+6·6°	1·4
50% H_2SO_4	~0°	~0°	~0°	~0°	~0°	4·5
conc H_2SO_4	−5·0°	−5·9°	−9·9°	−12·3°	−13·6°	5·5

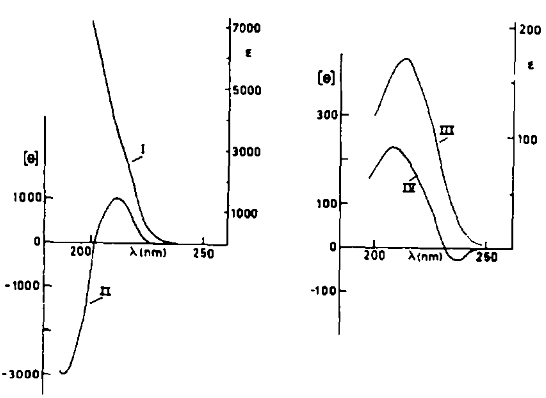


Fig 4.

especially polycyclic aromatic hydrocarbons—are best represented as reasonably flexible platelets, somewhat like a thin piece of wood, capable of undulations and bending modes. In addition to offering a reasonable explanation for the racemization mechanism of helicenes† (the bending is undoubtedly accompanied by stretching modes), the concept of flexible aromatic rings might provide new insight into properties (for example of nucleic acids) hitherto based solely on stiff, planar rings.

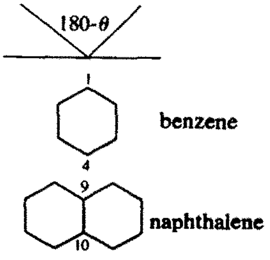
In what respect can the concept of flexible aromatic hydrocarbons influence our thinking about optical activity? A specific example will illustrate this best. The flexibility of polynuclear aromatic hydrocarbons made possible i.a. the synthesis of helicenes. With the resolution of helicenes an inherently dissymmetric chromophore absorbing above 200 nm because of π-π^* transitions was realized. The very high rotational strength allows minor deviation from planarity (of the helicene) to be easily detected. Optical activity might thus prove (as it has already proven in the case of helicenes) a useful tool for examining aromatic structures. In addition, contributions to the rotational strength of chiral centers, chromophores or structures by bent aromatics may well be significant. Thus the optical activity of a properly constructed paracyclophane (or other cyclophane) should vary considerably depending on the planarity or non-planarity of the aromatic ring. It would be of interest, to resolve a properly substituted [8] paracyclophane, carrying out a ring contraction following a method of Allinger[40] and carrying out a comparison of the rotational strength of these two compounds of equal optical purity.

CONCLUSIONS

One hundred years after Van't Hoff's proposals on the spatial orientation of atoms, stereochemists are still working on his ideas. If—some day in the not too distant future—a manned or unmanned space probe lands on Mars and signals to Earth—"there appears to be life here"—the information may well be based on the passage of light through an asymmetrically substituted tetrahedral carbon.

Table 4. Out of plane deformation energies (kcal/mol) for benzene and naphthalene

θ	ΔE^a	ΔE^b
0°	0	0
1°	0·029	—
2°	0·109	0·097
5°	0·671	0·609
10°	2·693	2·460
15°	6·092	—
20°	10·908	9·969



[a] Benzene, 1–4 bending
[b] Naphthalene, 9–10 bending

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