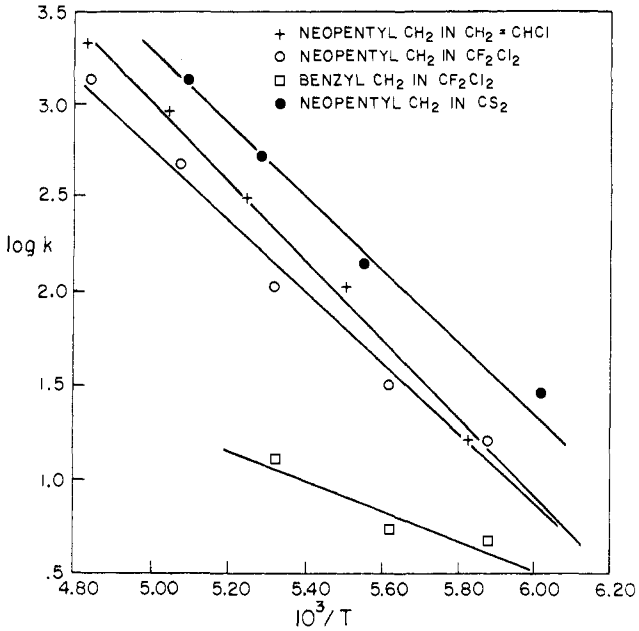

Figure 1. Rates of inversion about the neopentyl and benzyl nitrogen bonds in **4a**.

neopentyl and benzyl groups of **4a** dissolved in CF_2Cl_2. For the neopentyl methylene, $\Delta H^{\ddagger}_{298} = 8.4 \pm 0.5$ kcal/mol and $\Delta S^{\ddagger}_{298} = -4 \pm 8$ eu while for the benzyl methylene $\Delta H^{\ddagger}_{298} = 3.1 \pm 0.8$ kcal/mol and $\Delta S^{\ddagger}_{298} = -36 \pm 13$ eu. These results are plotted in Figure 1.

If the process causing nonequivalence of the methylene protons was due to slow nitrogen inversion one would expect similar barriers for **2** and **3**, which would be different from **1** and different again from dibenzylmethylamine. This is not observed.

Molecular models suggest that the barrier to rotation of the benzyl groups in **1**, **2**, **4a**, and dibenzylmethylamine should be small and should be very similar provided the phenyl ring remains perpendicular to the plane bisecting the benzylic protons. In fact, this common barrier should be no larger than that for the rotation of a methyl group (4.4 kcal/mol[4]). However, the restriction on the conformation of the benzyl group implies that rotation of a benzyl group will involve a large negative entropy of activation, as is observed.[8] There is no special orientation of the almost spherical neopentyl group which would allow it to rotate more easily and hence $\Delta S^{\ddagger}$ for rotation should be approximately zero for this group, again as observed. Furthermore, the barrier to rotation of the neopentyl groups in **3** and in **4a**, **4b**, and **4c** should be rather similar as is found.[9] For these reasons, we propose that the process causing nonequivalence of the methylene protons in the compounds discussed is hindered rotation[10] about the benzyl or neopentyl carbon–nitrogen bond. This must be true of the neopentyl group or else **4a** could not have different barriers for the neopentyl and benzyl groups. However, the possibility that inversion with $\Delta H^{\ddagger}_{298} \sim 3$–4 kcal/mol produces nonequivalence of the benzylic protons in these compounds cannot be entirely eliminated.

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[8] It is only because of the large negative entropy that the barrier to equivalence of the benzyl protons can be studied by nmr.

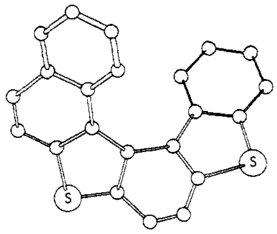
[9] For **4b** in CF_2Cl_2 $\Delta H^{\ddagger}_{298} = 6.0 \pm 0.4$ kcal/mol and $\Delta S^{\ddagger}_{298} = -10 \pm 12$ eu. For **4c** in CF_2Cl_2 $\Delta H^{\ddagger}_{298} = 6 \pm 2$ kcal/mol and $\Delta S^{\ddagger}_{298} = -1 \pm 9$ eu. The benzylic protons did not become nonequivalent in either compound.

[10] With hindered rotation as the rate-determining process rapid inversion is assumed each time a rotation occurs.[7]

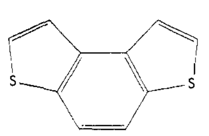
The Absolute Configuration of a Heterohelicene

Sir:

Recently the structure of the heterohelicene benzo[*d*]naphtho[1,2-*d'*]benzo[1,2-*b*:4,3-*b'*]dithiophene (I) has been elucidated by X-ray analysis.[1] The compound I along with a number of other heterohelicenes all having in common the benzo[1,2-*b*:4,3-*b'*]dithiophene moiety (II) have been resolved and the ORD and CD spectra have been measured.[2]



(−)- I



II

Knowing the structure of I we took the benzo[1,2-*b*:4,3-*b'*]dithiophene part of the molecule as a model compound[3] and applied the so-called dipole velocity method[4] to this molecule to calculate the absolute configuration. We found excellent agreement between the calculated and experimentally observed CD spectra (three longest wavelength bands). Our results showed that the (+)-heterohelicenes studied by us must have a right-handed helicity (a P configuration[5]). The absolute configuration of I has now been obtained independently by X-ray diffraction.

For the space group $P2_1$ of I, where the reflections *hkl* and $h\bar{k}l$ are Bijvoet pairs,[6] the intensities of the two members of a pair can be collected on one Weissenberg layer about the *a* or *c* axis. Structure factor calculations based on right-handed screws showed that clearly observable intensity differences should occur on the zero-, first-, and third-layer lines about the *c* axis, when taking the films with Cr radiation, $\Delta f''(\mathrm{s}) = 1.2$. The expected differences were indeed observed, but appeared to be opposite in sign from the calculated values in all cases where the difference was large. This clearly indicated the crystal to be composed of molecules having left-handed helicity (an M configuration[5]) in

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[1] G. Stulen and G. J. Visser, *Chem. Commun.*, 964 (1966).

[2] H. Wynberg and M. B. Groen, *J. Amer. Chem. Soc.*, **90**, 5339 (1968), and forthcoming papers.

[3] This simplification finds its justification in the fact that the CD spectra of all our heterohelicenes, varying from hexahelicenes up to an undecahelicene, were essentially similar.

[4] (a) A. Moscowitz, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1957; (b) C. M. Kemp and S. F. Mason, *Tetrahedron*, **22**, 629 (1966).

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

[6] J. M. Bijvoet, A. F. Peerdeman, and A. J. van Bommel, *Nature (London)*, **168**, 271 (1951).

contradistinction to the right-handed helicity used in the structure-factor calculations. The link between absolute configuration and optical rotation was made by dissolving the crystal (weighing *ca.* 0.01 mg) in chloroform (0.5 ml) and measuring the optical rotation. It was found to be −0.050° at 436 mμ and −0.025° at 546 mμ (Zeiss polarimeter, 5-cm cell). The anomalous dispersion experiment thus confirms the conclusions based on theoretical calculations: *the (+)-heterohelicene I has a right-handed helicity, the (−)-enantiomer a left-handed helicity.* This is the first time that the absolute configuration of a helicene has been established unambiguously. Attempts to determine the absolute configuration of Newman's hexahelicene[7] with various theories led to conflicting results.[4a,8] Our results, although not in contradiction with the other theories, strongly support the reliability of the dipole velocity method and therefore the assignment made by Moscowitz[4a] ((+)-hexahelicene having left-handed helicity).[9] With the same method Kemp and Mason[4b] assigned the right-handed helicity to (+)-1-fluoro-12-methylbenzo[*c*]phenanthrene (a "tetrahelicene").

Having established the absolute configuration of I we were able to assign the absolute configuration of our other heterohelicenes[2] on the basis of the similarity of their ORD and CD spectra. All heterohelicenes which we have studied thus far behave like I, a positive rotation being connected with right-handed helicity. We believe that the knowledge of the absolute configuration of I might also help in establishing the absolute configuration of other helicenes including hexahelicene by chemical and physical correlations (*e.g.*, by the quasiracemate method).

Acknowledgment. We gratefully acknowledge the considerable contribution to this work by Professor Dr. Aafje Vos.

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(7) M. S. Newman and D. Lednicer, *J. Amer. Chem. Soc.*, **78**, 4765 (1956).

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

(9) Professors A. Moscowitz and S. F. Mason have recently informed us that they believe a sign inversion has inadvertently occurred in their calculations on hexahelicene. Although this does not affect our work, it is pertinent to our comments concerning the helicity of hexahelicene. If in fact sign inversion has occurred all discrepancies between theories[4,8] are removed and (+)-hexahelicene also has a P configuration, a philosophically satisfying conclusion.

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The Effect of Solvent and Counterion on Trapping of Triphenylmethide Ion by Nitrobenzene

Sir:

We have previously reported[1] that the triphenylmethide–potassium ion pair intermediate in the potassium *tert*-butoxide catalyzed hydrogen–deuterium exchange of triphenylmethane may be efficiently trapped by a one-electron transfer to added nitrobenzene. To determine the effect of ion pairing on the relative rates of electron transfer and protonation, k_e/k_h, we have studied the effect of reaction variables which are known[2] to produce separated ion pairs or to weaken interionic attractions.[3]

When varying amounts of the aprotic polar solvent hexamethylphosphorictriamide (HMPA) were added to the reaction mixture we found that, relative to the amount of deuterium incorporated, smaller quantities of triphenylmethane were lost. The ratio k_e/k_h decreases by a factor of greater than 40 from 100% *tert*-butyl alcohol to 56% HMPA. A detailed kinetic study of the reaction was carried out in a medium of 30% HMPA and the results analyzed based on the following scheme. Competing reactions of the base

$$\begin{tikzcd}
(C_6H_5)_3CH \arrow[rr, "k_1"] \arrow[dr, "k_2"'] & & (C_6H_5)_3CD \arrow[dl, "k_3"] \\
& (C_6H_5)C\cdot &
\end{tikzcd}$$

with nitrobenzene[4] complicated the analysis, but with suitable corrections, consistent results were obtained showing $k_2/k_1 = k_e/k_h = 1.23 \pm 0.04$ in eight separate determinations over four half-lives. Values of k_e/k_h at this and other concentrations of HMPA are listed in Table I.[5]

Table I. Efficiency of Electron Transfer Relative to Protonation for Various Mixtures of *tert*-Butyl Acohol and HMPA at 50°

ROD[a]/C_6H_5-NO_2	% HMPA by wt[c]	k_e/k_h
55	0	10
46	11	5
17	11	12
16	22	3
31[b]	30	1.23 ± 0.04
38	35	0.6
20	56	<0.4
46	56	<0.2
25[a]	75	$<10^{-3}$

[a] Alcohol was $(CH_3)_3COD$ except for the last entry where it was CH_3OD. [b] Nitrobenzene-d_5 was used. [c] The remainder of the reaction mixture was 0.5 *N* KOR in DOR.

The last listing in the table involves a change in alcohol. In this mixture of HMPA and methanol–potassium methoxide which is comparable to potassium *tert*-butoxide–*tert*-butyl alcohol in basicity, no measurable amount of triphenylmethane was lost after conditions which represent many half-lives for the exchange reaction. The greater acidity of methanol may invalidate comparison of the two solvent–base systems; however, where differences in pK_a between

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(1) R. D. Guthrie, *J. Amer. Chem. Soc.*, **91**, 6201 (1969).

(2) D. J. Cram in "Fundamentals of Carbanion Chemistry," A. T. Blomquist, Ed., Academic Press, New York, N. Y., 1965, p 85.

(3) Some of these results have been presented earlier: R. D. Guthrie, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

(4) Nitrobenzene-d_5 was used as an acceptor in kinetic runs to avoid dilution of the deuterium pool by exchange (see R. D. Guthrie and D. P. Wesley, *J. Amer. Chem. Soc.*, **92**, 4057 (1970)); however loss of base and nitrobenzene remained a problem. All the assumptions made were tested, however, and shown to have only minor effects on the calculated values of k_e/k_h.

(5) A determination of the kinetic isotope effect k_2/k_3 was carried out at 0 and 30% HMPA using deuterated substrate. Values of 6.5 and 5.0 were found, respectively. A value of 5.0 was assumed at other concentrations. The exact value used does not appreciably affect k_e/k_h.