Tetrahedron Vol. 37, No. 20, pp. 3485 to 3490, 1981
Printed in Great Britain.

0040-4020/81/203485-06$02.00/0
© 1981 Pergamon Press Ltd.

NMR STUDIES OF CONFORMATIONS AND DYNAMIC PROCESSES—II

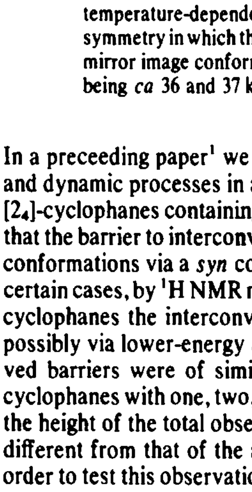
$[2_6]$BICYCLOPHANES WITH ETHYLENE BRIDGES

THOMAS OLSSON, DAVID TANNER, BENGT THULIN and OLOF WENNERSTRÖM*
Department of Organic Chemistry, Chalmers University of Technology and University of Göteborg, S-412 96 Göteborg, Sweden

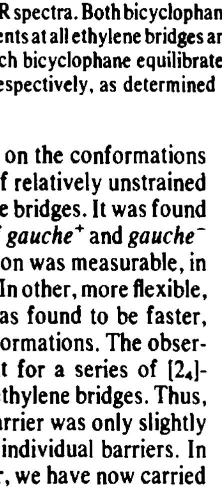
(*Received in UK* 11 *November* 1980)

Abstract—The conformations and dynamic processes in two bicyclophanes have been analysed on the basis of temperature-dependent ^{1}H NMR spectra. Both bicyclophanes are suggested to have a lowest-energy conformation of D_3 symmetry in which the substituents at all ethylene bridges are *gauche*$^+$ (or *gauche*$^-$) oriented. The interconversion of the mirror image conformers of each bicyclophane equilibrates the two hydrogens in each methylene group, the barriers being *ca* 36 and 37 kJ mol^{-1}, respectively, as determined by line-shape analysis.

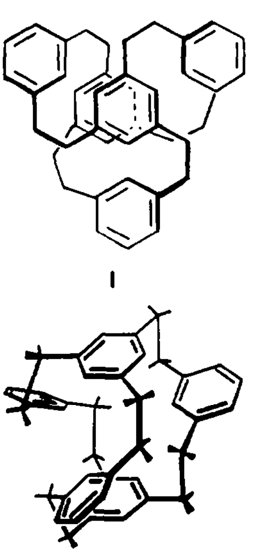
In a preceeding paper[1] we reported on the conformations and dynamic processes in a series of relatively unstrained $[2_4]$-cyclophanes containing ethylene bridges. It was found that the barrier to interconversion of *gauche*$^+$ and *gauche*$^-$ conformations via a *syn* conformation was measurable, in certain cases, by ^{1}H NMR methods. In other, more flexible, cyclophanes the interconversion was found to be faster, possibly via lower-energy *anti* conformations. The observed barriers were of similar height for a series of $[2_4]$-cyclophanes with one, two, or four ethylene bridges. Thus, the height of the total observable barrier was only slightly different from that of the assumed individual barriers. In order to test this observation further, we have now carried out the same type of temperature-dependent NMR study on the two bicyclophanes **1** and **2**, which contain six equivalent ethylene bridges.[2,3]

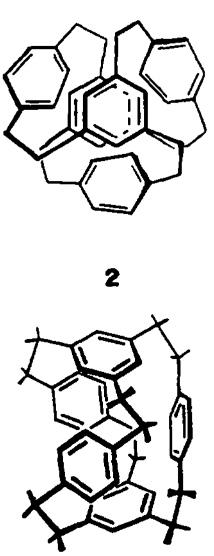


1



2





RESULTS AND DISCUSSION

The bicyclophanes **1** and **2** are less flexible than the $[2_4]$-cyclophanes discussed in the preceeding paper, but the same types of dynamic process are possible. Rotation of the *para*-substituted benzene rings can occur in **2** and the more important torsional motion about the sp^3-sp^3 C–C bonds in the ethylene bridges is possible in both bicyclophanes. There are six equivalent ethylene bridges in these species, all of which must have *gauche* orientation as *anti* orientations are ruled out for steric reasons. The four hydrogens in each bridge have different environments, but the interconversion of *gauche*$^+$ and *gauche*$^-$ conformations which must occur via *syn* conformations, equilibrates the four hydrogens into two sets of two. For both bicyclophanes, there are sixty-four (2^6) possible all-*gauche* conformers but only fifteen of these are different due to high molecular symmetry. As many of these conformers may be of similar energy and, as shown in Scheme 1, there are many possible routes for their interconversion, the analysis of such a complicated system is very difficult. However, since the equilibration of the geminal hydrogens in the ethylene bridges requires interconversion of mirror-image conformations via passage over six *syn* barriers, DNMR methods may be applicable. There is also always the possibility, however slight, that a single conformer is of substantially lower free energy than the rest and will thus dominate at low temperatures.

These relatively large and flexible systems also provide a further opportunity to find out whether a sequence of similar energy barriers, which can not be observed individually, will appear as one barrier which is similar in height to each individual barrier.

It can be shown by perturbation theory that conformations of high symmetry represent either local maxima or minima of the total energy of a molecule.[4] The highest conceivable symmetry for bicyclophanes **1** and **2** is D_{3h}, but such conformers are unlikely for steric reasons. However, the D_3 conformers of both bicyclophanes do seem to be favourable from inspection of CPK models.

Model studies also reveal that some of the possible conformations of bicyclophanes **1** and **2** define a central cavity large enough to function as a host for small guest or solvent molecules. Knowledge of the conformational equilibria and relative free energy of the conformers of the potential host molecule would reveal whether or not such complexation is to be expected.

The ^{1}H NMR spectrum of $[2_6]$-$(1,3,5)_2(1,3)_3$*bicyclophane*, **1**, in $CDCl_3$ or CD_2Cl_2 at 300 K is simple, due to the threefold axis of symmetry, and shows an AA'BB'-pattern, centred on δ 2.68, for the ethylene protons (see also Fig. 1) as expected for an average spectrum of several conformers which interconvert rapidly on the NMR time scale. The large upfield shift of the peaks

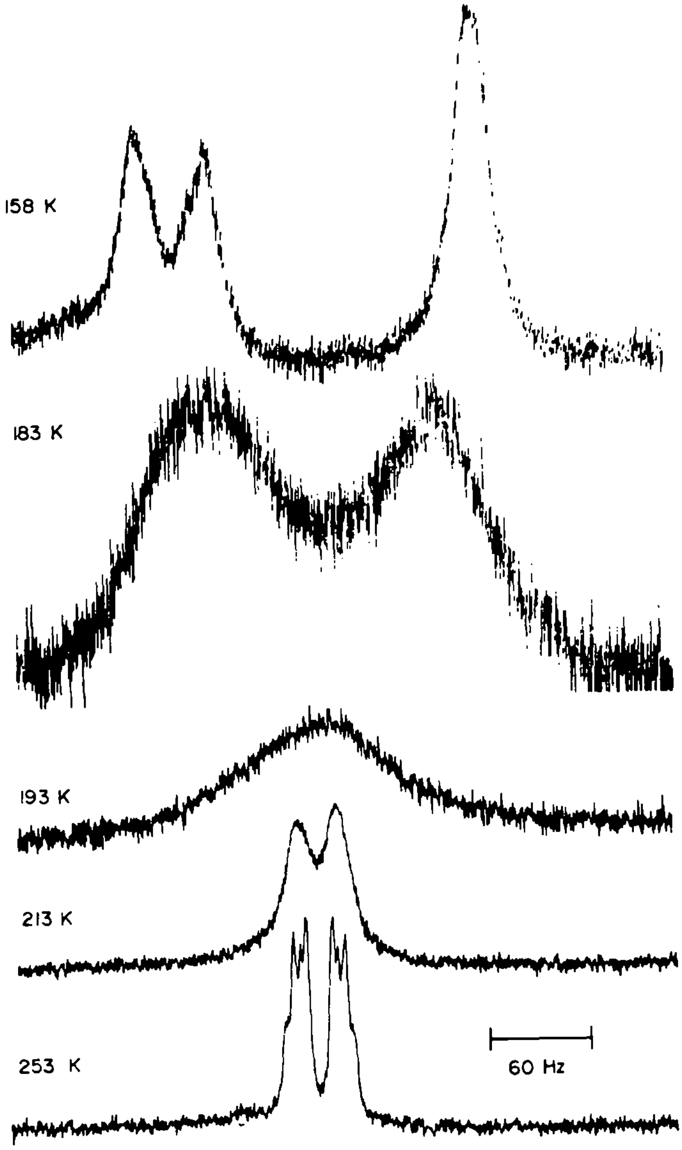


Fig. 1. 270 MHz 1H NMR spectrum of $[2_6](1,3,5)_2(1,3)_3$bicyclophane, 1, in CD_2Cl_2 at different temperatures. The ethylene region is shown.

from the aromatic protons of the trisubstituted rings (δ 6.36) and the protons between the bridges in the *meta* substituted rings (δ 6.05, see also Fig. 2) has been explained as being due to mutual shielding by the benzene rings in a rather compact conformation.[3] On cooling the sample in CD_2Cl_2 all signals broaden, and at temperatures below 185 K the ethylene signals resharpen to three peaks in the ratio 1:1:2 (Fig. 1). Simultaneously, the aromatic signals sharpen to the same pattern as observed in the average spectrum at room temperature and with the same coupling constants (Fig. 2). Some peaks of much lower intensity are also observed in the low-temperature spectrum, indicative of the presence of other, minor, conformers. However, the low-temperature spectrum is consistent only with the presence of a threefold axis of symmetry in the major conformer(s), that is, the D_3- and C_{3h} conformations shown in Scheme 1. In the latter, the *meta*-substituted rings are arranged perpendicular to the trisubstituted rings and no large shielding effects should be observed. The C_{3h}-conformer can thus be ruled out, and the strong shielding of the protons in the trisubstituted rings (δ 6.15) and the isolated protons in the *meta*-substituted rings (δ 5.73) at 158 K is better explained by assuming a compact D_3 conformation to be the most stable one. This conformer has no central cavity, and the structure is distinctly helix-like. Although the simple low-temperature spectrum could also be due to an average of several non-symmetrical conformations, depending on the relative magnitudes of the rate constants for the processes shown in Scheme 1, this explanation seems less likely.

In the bicyclophane $2,[2_6](1,3,5)_2(1,4)_3$*bicyclophane*, the *para*-substituted benzene rings which bridge the "top" and "bottom" of the molecule rotate freely, resulting in a singlet (δ 6.5) in the NMR spectrum for the protons on these rings. The trisubstituted rings also give rise to a singlet (δ6.65), as do the ethylene protons (δ 2.79, see also Fig. 3 and 4). The signals from the two types of ethylene proton are thus coincident at room temperature, and the observed spectrum is either due to a rapid averaging of several non-symmetrical conformers or that of essentially one symmetric conformer and its

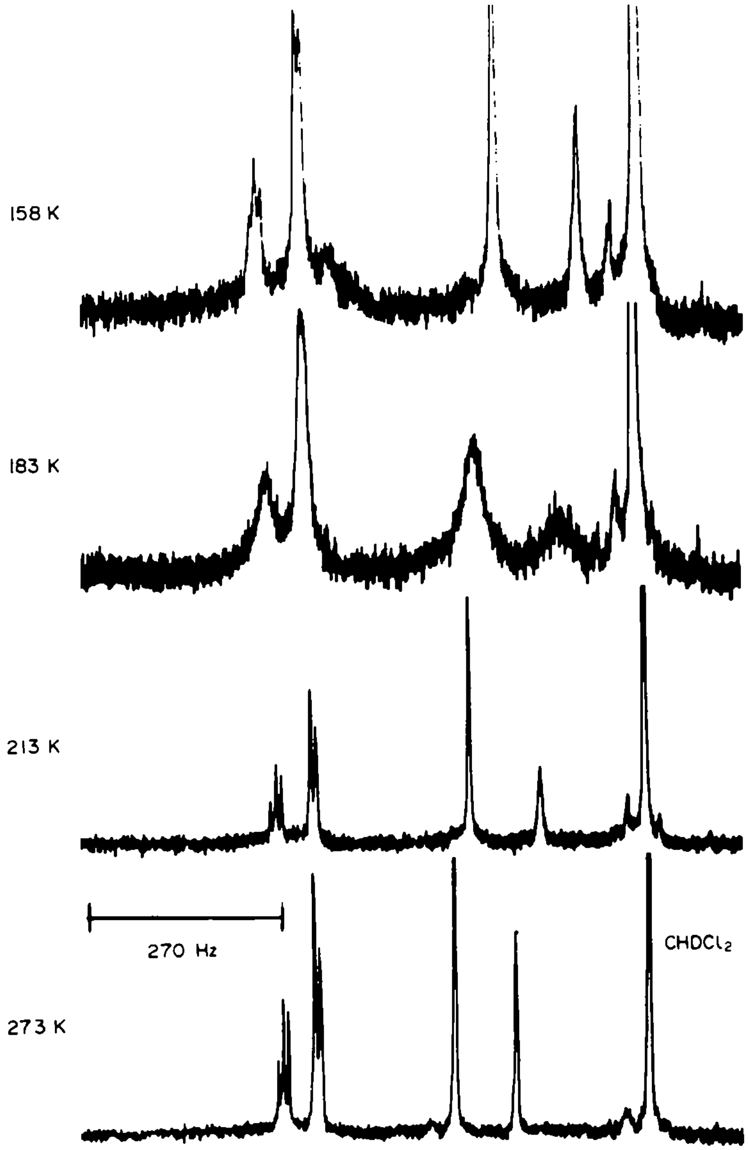


Fig. 2. 270 MHz ^{1}H NMR spectrum of $[2_6](1,3,5)_2(1,3)_3$bicyclophane, 1, in CD_2Cl_2 at different temperatures. The aromatic region is shown.

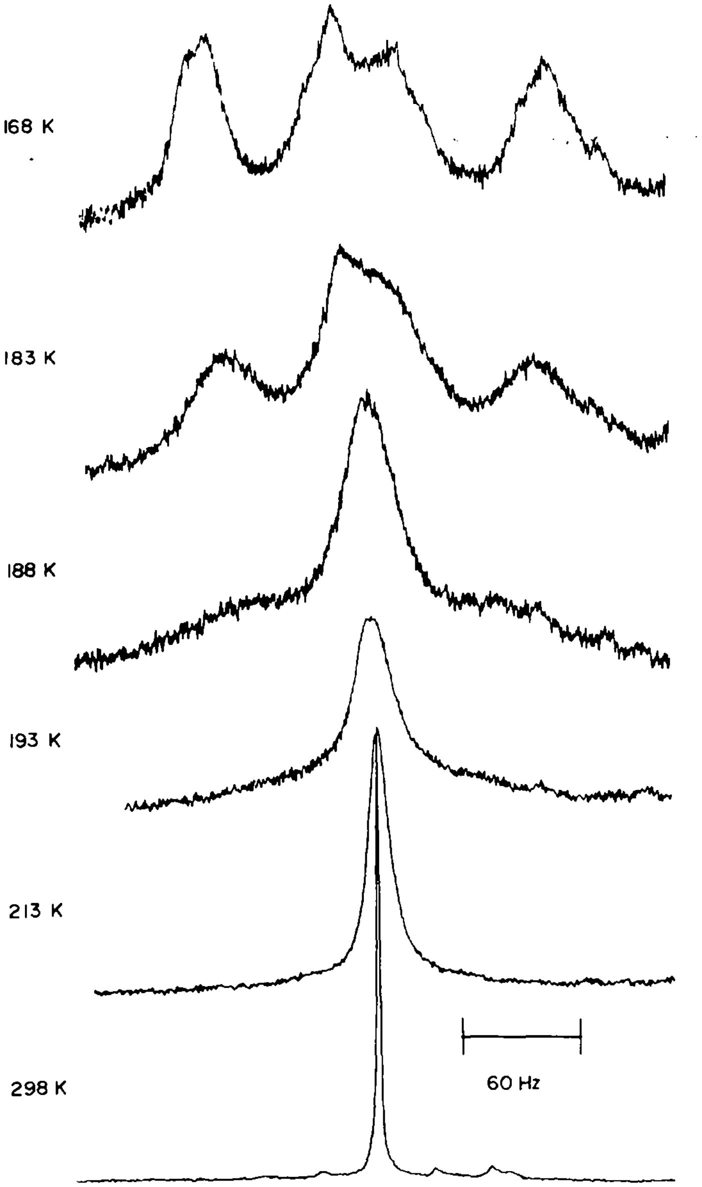


Fig. 3. 270 MHz ^{1}H NMR spectrum of $[2_6](1,3,5)_2(1,4)_3$bicyclophane 2, in CD_2Cl_2/acetone-d_6 at different temperatures. The ethylene region is shown.

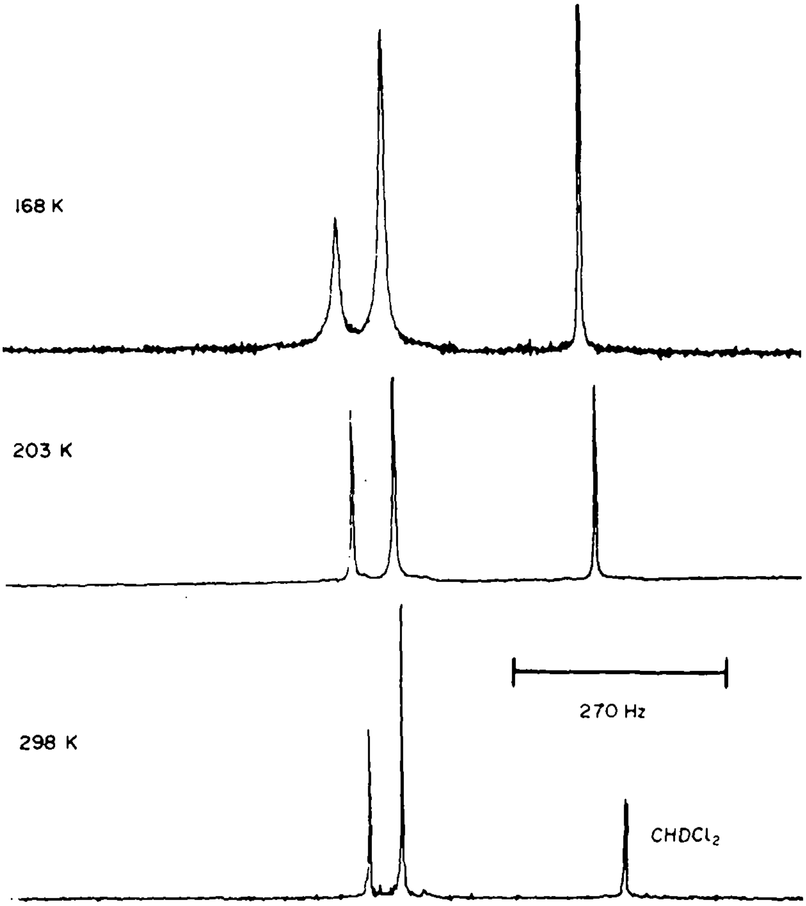
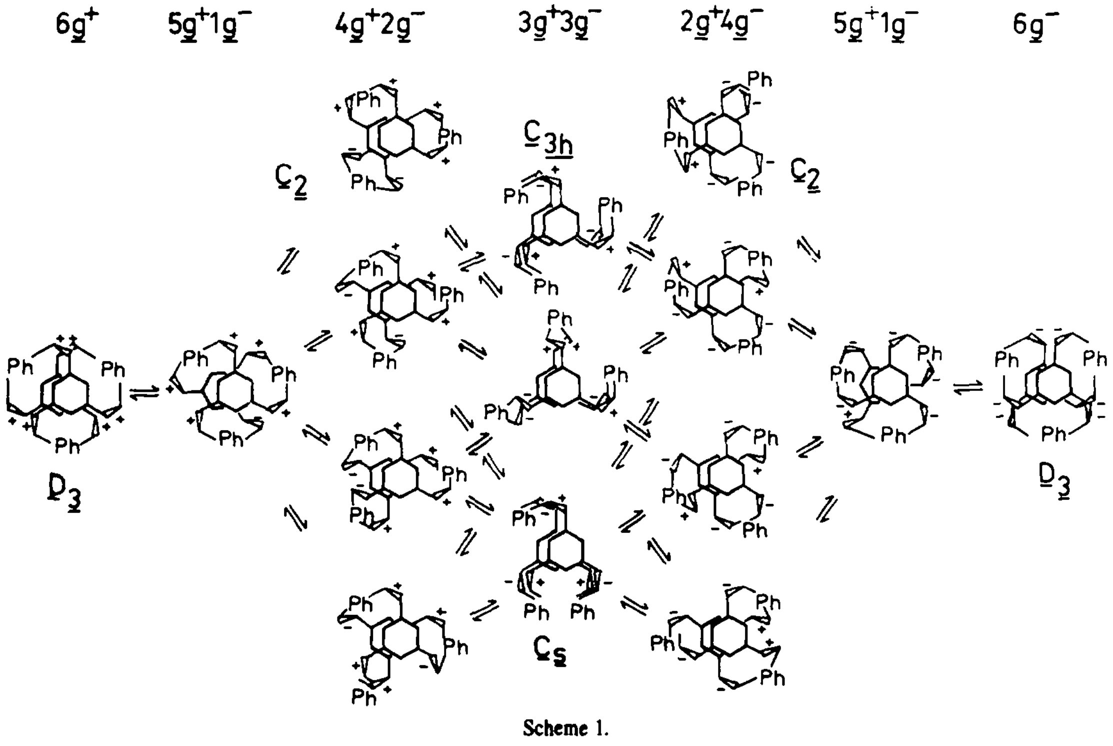


Fig. 4. 270 MHz ^{1}H NMR spectrum of $[2_6](1,3,5)_2(1,4)_3$bicyclophane, 2, in CD_2Cl_2/acetone-d_6 at different temperatures. The aromatic region is shown.



Scheme 1.

mirror image. The two singlets from the aromatic protons are shifted upfield due to mutual shielding, the effect being weaker than that observed for the inner protons in 1. On cooling the sample in CD_2Cl_2/acetone-d_6, the NMR spectrum changes gradually. The aromatic peaks broaden slightly, (Fig. 4) while the ethylene peak first broadens and then re-emerges as a pattern of four signals (Fig. 3) of which the outer two and the inner two each represent a pair of interconverting protons. The coalescence temperatures are slightly different for the two pairs. Although some further broadening of the aromatic signals is observed at low temperatures, the rotation of the *para*-substituted rings must be fast even at 170 K. The conformer(s) of lowest energy can not be as compact as those of bicyclophane 1 but the dominance of a single conformer (of D_3 symmetry) seems to occur also in this case. The conformers of high symmetry thus appear to represent energetic minima of both bicyclophanes.

The barriers were determined by line-shape analysis, employing visual comparison of calculated and measured spectra recorded at five temperatures between 172 K and 203 K, as described in the preceeding paper. The best fit was obtained with the following parameters assuming, in both cases, a low-temperature ABCD spin system changing to an AA'BB' system. For bicyclophane 1: $\Delta\nu_{AB}$ 200 Hz, $\Delta\nu_{AC}$ 40 Hz, $\Delta\nu_{AD}$ 200 Hz; $J_{AB} = J_{CD}$ −13 Hz, $J_{AC} = J_{AD} = J_{BC}$ 3 Hz, J_{BD} 12 Hz, relaxation time 1 s; for bicyclophane 2: $\Delta\nu_{AB}$ 170 Hz, $\Delta\nu_{AC}$ 70 Hz, $\Delta\nu_{AD}$100 Hz; $J_{AB} = J_{CD}$ −13 Hz, $J_{AC} = J_{AD} = J_{BC}$ 3 Hz, J_{BD} 12 Hz; relaxation time 1 s. The calculated barriers are 36 kJ mol^{-1} for bicyclophane 1 and 37 kJ mol^{-1} for bicylophane 2.

The barriers are thus similar in height to those observed in the simpler cyclophanes with one, two or four ethylene bridges described in the preceeding paper. Apparently, the same dynamic process is operating in all these cases and is identified as the torsional motion about the sp^3-sp^3 C—C bonds in the ethylene bridges with a transition state in which two aromatic substituents are *syn* oriented. If several barriers of the same type must be surmounted successively, the total barrier is only slightly higher than the individual ones.

Acknowledgements—We thank Dr. H.-E. Högberg for valuable discussions and Mrs. I. Raston for skilful technical assistance. Financial support from the *Swedish Natural Science Research Council* is gratefully acknowledged.

REFERENCES

1. T. Olsson, D. Tanner, B. Thulin, OL Wennerström and T. Liljefors, *Tetrahedron* **37**, 3473 (1981).
2. H.-E. Högberg, B. Thulin and O. Wennerström, *Tetrahedron Letters* 931 (1977).
3. H.-E. Högberg and O. Wennerström, manuscript submitted for publication.
4. R. Pearson, *Symmetry Rules for Chemical Reactions* p. 16. Wiley, New York (1976).