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SOME REMARKS ON HIGH-SYMMETRY MOLECULES. MOLECULAR STRUCTURE OF CIS AND TRANS 3,11-DIMETHYLDISPIRO[5,1,5,1]TETRADECAN-7,14-DIONE

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As well known, two or more atoms related by symmetry operations (rotation, reflection, inversion, improper rotation) are isochronous when observed by NMR spectroscopy in an achiral solvent (1)(2).

In order to determine the number of diastereotopic - and hence on principle anisochronous-atoms that are present in the molecules with symmetry other than C_1, it is convenient to employ the concept of submolecular asymmetric unit (3). By this expression we mean the portion of molecule inside which no symmetry relation exists. The asymmetric unit repeats in the molecule h times, h being the order of the symmetry point group of the molecule.

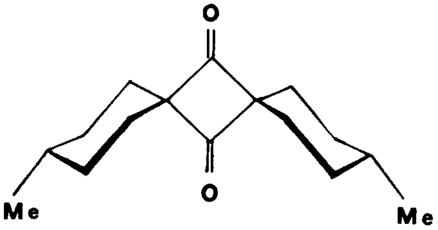
Furthermore, we can divide two classes of atoms depending on the position they have in respect of the elements of symmetry that are present in the molecule. According to the nomenclature used by crystallographers, an atom placed outside any element of symmetry is called atom in a general position. It repeats itself inside the molecule h times (2 for C_s, C_i, C_2; 3 for C_3; 4 for C_{2h}, C_{2v}, D_2, C_4, S_4, etc.). An atom placed on some element of symmetry is called atom in a special position. Its multiplicity inside the molecule is h/m, m being the number of symmetry operations (including identity) that may be carried out on the molecule leaving the position of the atom unchanged. The relative intensity of the peaks originated from each group of atoms in the NMR spectrum, apart from other factors, is proportional respectively to h and h/m.

Such observations rationalize and simplify the interpretation of the NMR spectra of high-symmetry molecules and are particularly important for the examination of the ^{13}C-NMR (CMR) proton decoupled spectra, where the number of lines should correspond to the number of carbons present in the asymmetric unit.

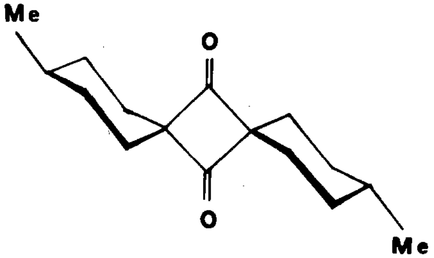
The detection of fewer lines than foreseen may be due to accidental coincidences, or to the apparent increase in symmetry connected with the presence of mobile molecules. In most cases, superposition of resonance lines of differ ent carbons is easily recognized and does not cause serious problems, but sometimes such a phenomenon does not allow the attribution of the molecular structure. In favourable cases, degeneracy may be removed by the use of a shift reagent, which increases the difference among diastereotopic atoms. On this regard, we wish to describe an example of structural attribution to two stereoisomers with a different symmetry and consequently different asymmetric units.

In view of the synthesis of macromolecules having non conventional structure, we were interested in the preparation and structural characterization of ketonic dimers of cyclic ketenes, as models of possible polymeric chains and as sources of high purity monomers.

4-Methylcyclohexancarboxylic acid chloride (a mixture of <u>cis</u>-<u>trans</u> isomers) was treated with Et_3N in boiling toluene. Formation of ketene was evidenced by an intense yellow colour, but the product further reacted under the reaction conditions to give a mixture of <u>cis</u> and <u>trans</u> 3,11-dimethyldispiro[5,1,5,1] tetradecan-7,14-dione (I and II) with yields above 90%.



I <u>cis</u> C_{2v}



II <u>trans</u> C_{2h}

The two isomers were separated by fractional crystallization. The chemical structure of both compounds was determined by mass spectrometry (molecular peak at 248 m/e, base peak at 124), NMR and IR; however the spectroscopic behaviour being almost identical, stereochemistry could not be determined. The examination of the ^{1}H-NMR spectra run at 100 MHz in the presence of $Eu(fod)_3$-d_{27} allows the assignment of all peaks and the determination of the coupling constants. Spectra are clearly differentiated, but the differences could not be interpreted in terms of the two structures.

On the basis of the above discussion the two isomers should clearly have different CMR spectra. The asymmetric unit of the <u>trans</u> isomer (point group

C_{2h}) contains two methylenes in a general position (with multiplicity 4) and other four carbon atoms on the mirror plane (and therefore with multiplicity 2). Its CMR spectrum should therefore exhibit 6 resonance lines, whereas that of the cis isomer (point group C_{2v}) should exhibit 7 lines, owing to the non equivalence of the two carbonyl groups, each of them having multiplicity 1.

The CMR spectrum run at 22.63 MHz in hexadeuterobenzene exhibits 6 lines in both cases, with virtually identical frequencies and intensities. However, the non equivalence of the two carbonyl groups of the cis isomer is clearly evidenced when the spectrum is run in the presence of Eu(fod)$_3$ (Table 1).

Table 1

CMR Spectra of 3,11-Dimethyldispiro[5,1,5,1]tetradecan-7,14-diones.

attribution	cis isomer	trans isomer
$\underline{C}H_3$	22.0 δ	22.0 δ
$\underline{C}H_2$	29.0	29.1
$\underline{C}H_2$	30.5	30.7
$\underline{C}H$	31.6	31.6
$\underline{C}$	73.9	74.0
$\underline{C}=O$	214.1°	214.0°°

° split in two lines at 214.7 and 217.4 δ in the presence of Eu(fod)$_3$;

°° shifted, but not split in the presence of Eu(fod)$_3$.

It has been thus possible to ascertain that the compound melting at 117°C, which is more abundant (in the ratio 55/45), more soluble and has a higher retention time (LAC-3R-728, 150' x 0.01", 150°C), is the cis isomer, whereas the trans isomer melts at 163°C.

Analyses of molecular symmetry by CMR for the solution of structural problems have already been carried out by several authors (4). However, in the examples dealt with so far, the differences among asymmetric units of the structures under consideration were quite remarkable. The case described here probably represents the most subtle example of structural attribution by symmetry criteria, carried out without using diffractometric methods. More generally, we believe that the concepts and the nomenclature introduced by us might lead to a more general use of such criteria. In the near future, we will refer on their application to a large family of polycyclic hydrocarbons.

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