RING INVERSION BARRIER IN THE $S_1(n\pi^*)$ STATE OF *cis*-3,4-DIMETHYL CYCLOPENTANONE

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Dedicated to the memory of Günther Snatzke.

Abstract: By means of Circular-Polarization-of-Luminescence (CPL) spectroscopy, *cis*-3,4-dimethyl-cyclopentanone is shown to consist of rapidly interconverting enantiomeric half-chair conformers. The barrier to ring inversion in the $S_1(n\pi^*)$ state is determined to be 12 ± 1.5 kJ/mol.

Introduction

Replacement of a methylene group in cyclopentane by a carbonyl moiety, so as to yield cyclopentanone, results in the introduction of (i) a difference in energy between the half-chair and envelope conformations and (ii) a barrier to pseudorotation.

In cyclopentanone (CP) the stable conformations are the two equivalent half-chair forms having C_2 symmetry, as has been shown by a microwave study[1]. The bending mode is lower in frequency than the twisting mode so that ring inversion occurs through the planar ring which is *circa* 750 cm^{-1} (9 kJ/mol) higher in energy[2,3]. The introduction of two vicinal methyl substituents in cyclopentane with a *cis*-1,2 relationship, also favors the half-chair conformation[4]. It therefore has to be expected that *cis*-3,4-
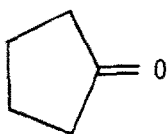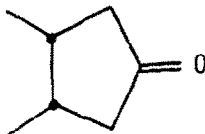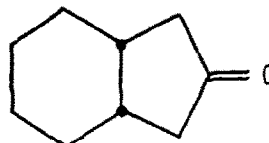

CP   DMCP   BCN

dimethylcyclopentanone (DMCP) occurs as a very fast dynamical equilibrium of the two half-chair conformers. The two conformers are enantiomers, and so their interconversion is a racemization process which can be experimentally studied using Circular Polarization of Luminescence (CPL) spectroscopy.

CPL is the emission analogue of circular dichroism[5,6]. In CD one measures - for an enantiomerically pure compound - the difference of the absorption coefficients of left (L) and right (R) circularly polarized light, $\Delta\epsilon = \epsilon_L - \epsilon_R$; in CPL the unequal amounts of L- and R-polarized photons in the molecular luminescence (fluorescence or phosphorescence), $\Delta I = I_L - I_R$. The chiral discrimination in the absorption process is conveniently characterized by the dissymmetry factor g ($= \Delta\epsilon/\epsilon$), that in the luminescence by $g_{lum} = \Delta I/I$. Here ϵ (I) denotes the average absorption coefficient (emission intensity) for L and R light, $\epsilon = (\epsilon_L + \epsilon_R)/2$ (I=$(I_L + I_R)/2$). The type of information which is acquired is similar but complementary. Well-known is the utility of the CD technique in the study of absolute configuration and conformation of molecules - a field Snatzke contributed to in a visionary and masterly way. CPL probes molecular geometry as well - not that of the electronic ground state, but of the lowest excited singlet state[7] or triplet state[8]. In case the electronic excitation does not affect molecular geometry, the information from both chiroptical techniques is similar. Occasionally, however, excitation can lead to considerable distortion, in particular with small chromophores (i.e. localized transitions) or with flexible chromophores.
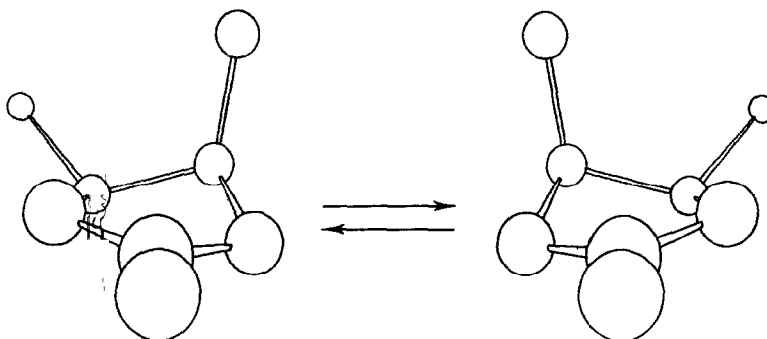
Half-chair forms of DMCP

An interesting situation arises when in an experiment the CD and CPL effects are combined. Then it is possible to probe the optical activity of racemic mixtures without the need of chemical resolution[9-11]. In such experiments the CD effect is employed to create an excess of one enantiomer in the excited state by irradiating the racemic sample with circularly polarized light. Consequently, the enantiomeric excess in the luminescent state is manifested by the emission of (partially) circularly polarized light. The technique also can be used for the direct determination of optical purity[12] and it opens a way to study the dynamics of fast racemization reactions, e.g. in the case of DMCP.

Results

A 0.03 M solution of *cis*-3,4-dimethylcyclopentanone (Wiley Organics) in a 1:1 mixture of methylcyclo-pentane and methylcyclohexane, contained in a cryostat was excited with circularly polarized light of wavelength 290 nm (spectral bandwidth 20 nm). Circular polarization was effected by passing the light through a Glan polarizer followed by a suitable quartz quarter-wave plate. The incident polarization was switched between left and right handedness by rotating the quarter-wave plate over 90°. In both modes the degree of circular polarization was determined to be 94 %. The use of high and equal modulation depths is advisable to avoid artefacts in the CPL measurements due to linear polarization effects[13]. That such artefacts are absent indeed was demonstrated by performing the CPL measurements with the achiral ketone adamantanone: within experimental error the observed CPL signals were always zero.
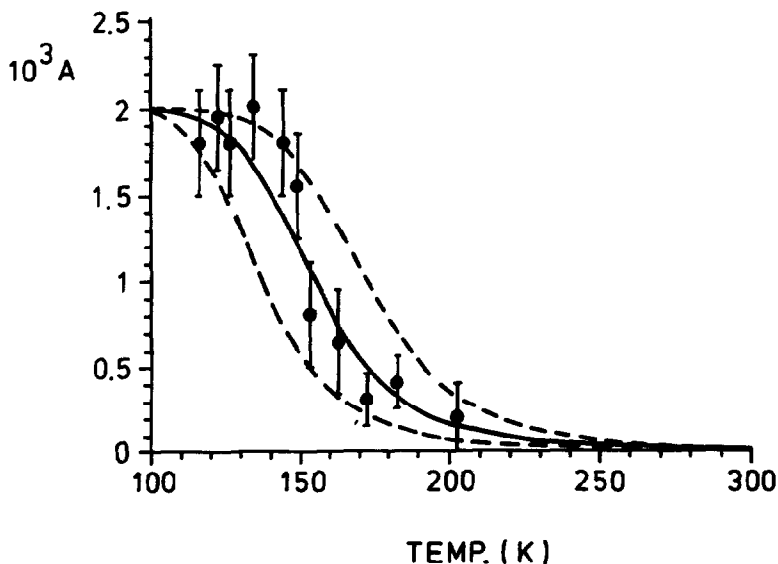

Figure 1

The circular polarization of the fluorescence of DMCP was observed at 420 nm with a bandwidth of 20 nm, with the photon-counting instrument described previously[14]. The results are given in figure 1, which displays, as a function of temperature, the differential CPL signal observed (that is, the degree of circular polarization in the fluorescence obtained with L-excitation light *minus* that with R light). At room temperature the effect is zero within experimental error (1 x 10^-4). Upon cooling the sample, the CPL signal gradually increases to reach a plateau value at about 120 K.

Qualitatively the result can be interpreted as follows: At the high temperatures, the racemization

rate in the excited state, k*, is large as compared with the reciprocal lifetime τ_F^{-1} of the fluorescent state, and consequently the effect of the chiral photoselection is vanished before the emission event occurs. Lowering the temperature will hardly affect τ_F^{-1} but will lead to decrease of k*. In the medium temperature region of figure 1, the rate of ring inversion is sufficiently slowed down to enable observation of some optical activity, whereas at temperatures near 125 K the maximum CPL effect, A_0, can be detected.

Quantitatively, the magnitude of the differential CPL signal, A, as a function of temperature is given by

$$A/A_0 = [2 \, k^* \, \tau_F + 1]^{-1}$$

where k* is given by the Eyring equation

$$k^* = (kT/h) \exp (-B^{\neq}/RT)$$

Using $\tau_F = 1.9$ ns[15] and $A_0 = 20 \times 10^{-4}$ (plateau value in Figure 1), we find from a fitting procedure that the energy barrier, B*, lies in between 13.5 and 10.5 kJ/mol (these values correspond with the broken lines in figure 1). So, in the excited state the barrier to ring inversion equals 12 ± 1.5 kJ/mol.

We note that sign and order of magnitude of A_0 which we find from the plateau value in figure 1, completely agree with expectation: From theory, the differential CPL in the absence of racemization is equal to the product of the dissymmetry factors in absorption and emission, i.e. $A_0 = g \cdot g_{lum}$. Obviously, for DMCP the individual dissymmetry factors are not experimentally accessible. For enantiomerically pure trans-bicyclo[4.3.0]non-3-en-8-one we have determined g and g_{lum} separately; the product of multiplication indeed is[16] $+2 \times 10^{-3}$. This ketone can serve as a model compound for enantiomerically resolved DMCP because in substituted cyclopentanones, sign and magnitude of the $S_0 \rightarrow S_1(n\pi^*)$ Cotton effect is controlled predominantly by the chirality of the five-membered ring[17]; in Snatzke's classification these compounds exhibit dissymmetry in the second sphere[18].

Discussion

The mere fact that a nonvanishing value of A is observed, unambiguously shows that the preferred conformers of cis-3 4-dimethylcyclopentanone must include chiral ones - in the ground state as well as in the $S_1(n\pi^*)$ state. Furthermore, from the fact that the magnitude of the observed optical activity is equal to that of a ketone in which the carbonyl group is contained in a twisted cyclopentane ring, it can be concluded that the two half-chairs are predominating the conformational equilibrium (the reasonable assumption is made that other conceivable conformers, such as envelope-forms, do not have much smaller fluorescence quantum yields).

Data on ring inversion barriers of carbonyl compounds in the excited state are scanty. We have

previously studied[16] the related species cyclopentanone and *cis*-bicyclo[4.3.0]nonan-8-one (BCN) and found the values of B* to be smaller than *circa* 8 kJ/mol and larger than 33 kJ/mol, respectively. One should be cautious in applying ground state conformational analysis arguments to molecules in excited states because electronic excitation can profoundly change shape and position of the potential energy hypersurface as a function of the nuclear coordinates. In the case of CP, DMCP and BCN, however, a comparison is warranted: not only is the excited state involved of the same type [$S_1(n\pi^*)$], but the associated excitation energy is also largely confined to the carbonyl group. The observed order of the barriers B*, CP < DMCP < BCN, agrees with expectation. The bicyclic compound has the highest barrier because inversion of the five-membered ring requires concomitant inversion of the cyclohexane ring. Assuming similar pathways, the barrier of DMCP should be higher than that of cyclopentanone because of larger eclipsed bond interactions.

Because in CP the barrier in the $S_1(n\pi^*)$ state is smaller than *circa* 8 kJ/mol, it was concluded[16] that upon electronic excitation, the ring-inversion barrier decreases but the magnitude of this decrease could not be deduced. Now it is possible to specify the magnitude of this decrease in more detail. From jet-cooled fluorescence excitation spectroscopic data Laane et al. have found[19] that the ring-bending frequencies of cyclopentanone in the S_0 and S_1 states differ only slightly: 95 and 92 cm^{-1}, respectively. These data indicate that the rigidity of the ring is not very much affected by excitation. We propose therefore that in cyclopentanone the barriers B* and B are approximately equal, and that a similar situation holds for substituted cyclopentanones.

Sablayrolles et al. deduced[20] a barrier height for ring inversion of 9.0 kJ/mol from a low-frequency mode in the Raman spectrum of DMCP. This result is compatible with ours only if the barrier to ring inversion increases upon excitation with 3 kJ/mol. Moreover it implies that the ground state barriers of DMCP and CP are equal, which is against expectation. If in the ring inversion process DMCP and CP follow similar pathways, then the increase of barrier height upon methyl substitution can be approximated by the difference in interaction energy of eclipsing C-Me groups and eclipsing C-H bonds. A rough measure for the effect may be taken from the rotational barriers of ethane and butane[21], which yields 2.5 kJ/mol (3.6 *minus* 3.0 kcal/mol).

It would be interesting to extend the present study to a series of *cis*-3,4-dialkylcyclopentanones, and to include the ground state barriers by using dynamic NMR experiments. This would enable a more exacting check whether with cyclopentanones the barriers in ground and excited state are approximately equal. The availability of B* values of a homologous series, would allow one to study the coupling of the ring-inversion mode with the local carbonyl out-of-plane distortion in the $S_1(n\pi^*)$ state. Time-resolved CPL studies would be particularly interesting. Such measurements which are feasible on the *sub*-ms[22,23], and even on the *sub*-μs[24], but not yet reportedly on the ns time scale, can yield enthalpy and entropy of activation parameters for racemization reactions in excited states more directly[22].

References and notes

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