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Chirality Solely Due to the Presence of an Excited State**
By E. W. Meijer* and Hans Wynberg

One of the most fascinating challenges in the study of optical activity is the synthesis of a compound in which the optical activity is solely due to the presence of an excited state. This property is available in meso compounds with two identical chroomophores, in which one of the chroomophores is selectively excited. In the case of diketones with a plane of symmetry in the ground state, the chirality in the excited state is due to the out-of-plane geometry of one of the two carboxyl groups. We have focused our attention on 2,4-adamantanediol 3, whose chiral excited state is 1*.

The only way to obtain 1* in a high enantiomeric excess is by selective excitation of one of the two carboxyl groups of 1 by chemical conversion. The enantiomeric excess via a photochemical process is expected to be low, since the difference in absorption of right (or left) circular polarized light by the two carboxyls is governed by the dissymmetry factor in absorption. Obviously, resolution of an excited-state diketone belongs in the realm of fantasy.

Chemiluminescence of ketones is well known to occur via the decomposition of 1,2-dioxetanes [1-6]. A high yield of singlet-excited-state adamantane is obtained from the 1,2-dioxetane of 2-(methoxymethylene)adamantanone [7]. The chemical route towards optically active 1* via the optically active 1,2-dioxetane 3 is based on our previous work [5-8].

The optical precursor of 3 is enol ether 2. The latter is prepared in several steps from adamantane via the resolution of endo-bicyclo[3.3.1]non-6-ene-3-carboxylic acid [8]. A photooxygenation with O2 at -50°C, followed by rapid low-temperature column chromatography, afforded a solution of 1,2-dioxetane 3 in dichloromethane.

The ketodioxetane 3 was not stable enough to allow a structure determination. However, dilute solutions of 3 in n-heptane yielded chemiluminescence, (λmax = 420 nm, characteristic of ketone fluorescence) when heated. The product, which could be isolated in almost quantitative yield proved to be 2,4-adamanetanedione 1. It is reasonable to assume that the chemiluminescence is obtained from the decomposition of 3, which generates 1 in the excited state.

The enantiomeric excess of 3 is assumed to be identical to that of the resolved starting material, to wit ee = 69%. Therefore it is expected that in the formation of 1* one of the two carboxyls is excited in favor over the other in an enantiomeric excess of 69%.

This synthesis of chiral 1* is, to the best of our knowledge, the first example of a chemical route to a chiral compound (with high ee) whose chirality is solely due to the presence of an excited state.

The synthesis of 1* is one challenge, the detection of optical activity in this short-lived molecule is another. It seemed obvious to measure the circular polarization of chemiluminescence (CPCL) in the thermal activation of 3 [9]. However, the CPCL measurements of 3 (10^-3 - 10^-6 mol L^-1 in n-heptane) showed complete lack of optical activity at the moment of emission (g_{chemi} = 0 ± 3 x 10^-3).

This is probably caused by a fast racemization in the singlet-excited state. This racemization occurs by an energy transfer between the two carboxyls in the rigid conformation of 1*. This fast energy transfer in 1* is reasonable due to the close proximity of the two carboxyls. The UV spectrum of 1 and the CD spectrum of its mono-O analogue even indicate some π overlap of these chroomophores [7]. The intramolecular nπ* energy transfer is fast relative to the lifetime of a singlet-excited-state ketone, pointing to a rate of energy transfer of k_{ET} = 1 x 10^10 s^-1. Energy transfer between carboxyl nπ* excited states is a very intriguing phenomenon and several systems have been investigated [10-12] showing both efficient and slow processes. Recently, the circular polarization in fluorescence was studied after excitation of meso diketones with circular polarized light, [13] indicating a very efficient energy transfer for carbonyl groups in close proximity to each other. Although triplet-triplet annihilation may be regarded as another source of racemization in the excited state, it is assumed to be of minor importance. This is based on both the reaction conditions used and the fact that up to now the occurrence of this phenomenon in 1,2-dioxetane chemiluminescence has not been reported.

From the preliminary results presented here we can conclude that a synthesis of a compound that is chiral solely in its excited state can be performed by chemiexcitation of a meso diketone via an optically active 1,2-dioxetane. In order to obtain stability with respect to racemization it is necessary to increase the distance between the two chromophores. This type of compound would enable us to investigate the rate of intramolecular energy transfer.

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