at δ 1.95 ($W_{1/2}$ = 1.4 Hz) which broadens slightly at −113° ($W_{1/2}$ = 3.0 Hz). Further cooling causes viscosity broadening and ultimate precipitation at *ca.* −125°. Since it is likely that **1a** assumes a ground-state conformation of S_4 symmetry, the methyl groups are necessarily isochronous, as found. However, substitution of a 1-naphthyl group for one of the *o*-tolyl groups (**1d**)[5] lowers the molecular symmetry to C_s or C_1 and thus introduces the potential for anisochrony. Indeed, although the ^{1}H nmr spectrum of **1d** in CS_2 also displays a sharp singlet for the methyl protons at ambient temperature (δ 1.89), this signal broadens at lower temperatures and splits into two lines at δ 1.74 and 1.95 in the intensity ratio of 1:2 (T_c = −14°, $\Delta\nu$ = 13.0 Hz). Further cooling causes splitting of the more intense peak to a 1:1 doublet (T_c = −40°, $\Delta\nu$ = 1.25 Hz). Theoretical line shapes in agreement with those observed experimentally were calculated using a random exchange matrix to describe the methyl group permutations.[6] The calculated $\Delta G^{\ddagger}_{-14}$ is 13.5 kcal/mol. Further detailed comment on the processes responsible for this dnmr behavior is deferred to a general paper on the static and dynamic stereochemistry of tetraaryl systems of type Ar_4Z.

What is the relevance of this finding to the main question of conformational mobility in **1a**? In a previous and related study on conformational dynamics in triarylborane systems,[7] it was found that with respect to hindrance of rotation about the bond linking the aryl group to the central atom, the steric effect of the benzo substituent appears to be only slightly less than that of the *o*-methyl substituent. Accordingly, on the assumption that the ground-state conformations of **1a** and **1d** are similar, we may estimate the barrier of the former at not much above 13.5 kcal/mol, and an upper limit of *ca.* 16 kcal/mol may be placed with confidence.

Related tetraarylborate salts[8] show parallel dnmr behavior. Compound **2a** in CD_3OD exhibits a singlet (δ 1.59) for the methyl protons down to *ca.* −55°, below which viscosity broadening becomes severe. The presumed S_4 symmetry is reduced by substitution of an *o*-anisyl group for one of the *o*-tolyl groups (**2b**). This compound in CD_3OD shows partial splitting of the *o*-methyl resonance even at ambient probe temperatures. An increase in temperature causes coalescence to a singlet (δ 1.61), whereas cooling brings about splitting to a sharp 2:1 doublet, δ 1.53 and 1.59 (T_c = 42°, $\Delta\nu$ = 3.4 Hz). The calculated $\Delta G^{\ddagger}_{42}$ is 17.7 kcal/mol.[6] By contrast the analogous silane **1e**[9] shows partial splitting of the C–CH_3 proton signal only at temperatures below *ca.* −80° reflecting the smaller steric effect of *o*-methoxy relative to *o*-methyl and benzo substituents.

The increase in barrier height on going from the silicon to analogous boron systems is entirely consistent with the expected increase in steric congestion in the transition state when bonds to the central atom are shortened.[10] A similar correlation between bond lengths and barriers to aryl group rotation in trimesityl compounds of group Va elements has previously been noted.[13]

Granted an upper limit of 16 kcal/mol for the rotation barrier in **1a**, the estimated half-life of a stereoisomer at 25° is no more than 0.06 sec.[14] We are therefore forced to conclude that the barrier to interconversion of stereoisomers in the tetra-*o*-tolylsilane system is much too low to permit separation and isolation of stereoisomeric conformers of this compound at practicable working temperatures. In confirmation of this conclusion, all of our attempts to repeat the earlier work claiming the isolation of four, or possibly five, stereoisomers (mp 145, 228, 300, 344°; 270°)[2] have invariably led to a single isomer, mp 228–230°, and to no others.

It was originally stated,[2] without further detail, that "the aromatic groups of tetra-*o*-tolylsilane are not free to rotate about the carbon–silicon bonds and it is possible to construct no fewer than eight models of the molecule, representing four meso compounds and two racemic pairs." In an elaboration of this conclusion, Cahn, Ingold, and Prelog, on the assumption of a threefold potential for rotation about the C–Si bonds, calculated that nine isomers (three meso forms, three racemates) were possible.[15] The present work voids the experimental basis for these conclusions.[16]

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[5] Compound **1d** (mp 229–230°)[4] was prepared in 25% yield from the reaction of **1c** and 1-naphthyllithium in ether.

[6] The computer program employed was adapted from one developed by M. Saunders: see M. Saunders in "Magnetic Resonance in Biological Systems," A. Ehrenberg, B. C. Malmström, and T. Vänngård, Ed., Pergamon Press, New York, N. Y., 1967, p 85. We are grateful to Professor Saunders for providing us with a copy of his program.

[7] J. F. Blount, P. Finocchiaro, D. Gust, and K. Mislow, *J. Amer. Chem. Soc.*, **95**, 7019 (1973).

[8] Prepared by adaptation of literature procedures; see G. Wittig and W. Herwig, *Chem. Ber.*, 88, 962 (1955).

[9] Compound **1e** (mp 216–217°)[4] was prepared in 82% yield from **1c** and *o*-anisyllithium. Nmr in CS_2 δ 1.89 (s, 9 H), 3.18 (s, 3 H).

[10] In the solid state, the relevant bond lengths have been determined as *ca.* 1.64 Å in Ph_4B^- salts[11] and *ca.* 1.86 Å in some phenylsilane derivatives.[12]

[11] (a) M. Di Vaira and A. Bianchi Orlandini, *J. Chem. Soc., Dalton Trans.*, 1704 (1972); (b) C. Floriani, F. Calderazzo, and L. Randaccio, *J. Chem. Soc., Chem. Commun.*, 384 (1973).

[12] (a) P. C. Chieh and J. Trotter, *J. Chem. Soc. A*, 1778 (1969); (b) C. Glidewell and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 2409 (1972).

[13] A. Rieker and H. Kessler, *Tetrahedron Lett.*, 1227 (1969).

[14] Calculated from the Eyring equation, assuming $\Delta S^{\ddagger} = 0$.

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

[16] These considerations underscore the need for the caveat, repeatedly expressed,[7,17] that space-filling molecular models grossly exaggerate the energy requirements for the conformational interconversion of compounds of this type.

[17] H. Kessler, A. Moosmayer, and A. Rieker, *Tetrahedron*, **25**, 287 (1969).

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Optical Activity Due to Isotopic Substitution. Circular Dichroism of (1*R*)-[1-^{2}H]-α-Fenchocamphoronequinone

Sir:

The successful synthesis of (1*R*)-2-^{18}*O*-α-fenchocamphoronequinone (I), a molecule which owes its chirality to ^{16}O–^{18}O asymmetry, has revealed a CD spectrum which differs markedly from the spectra of other optically active α-diketones.[1] Therefore it became of

[1] W. C. M. C. Kokke and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, **94**, 7583 (1972).

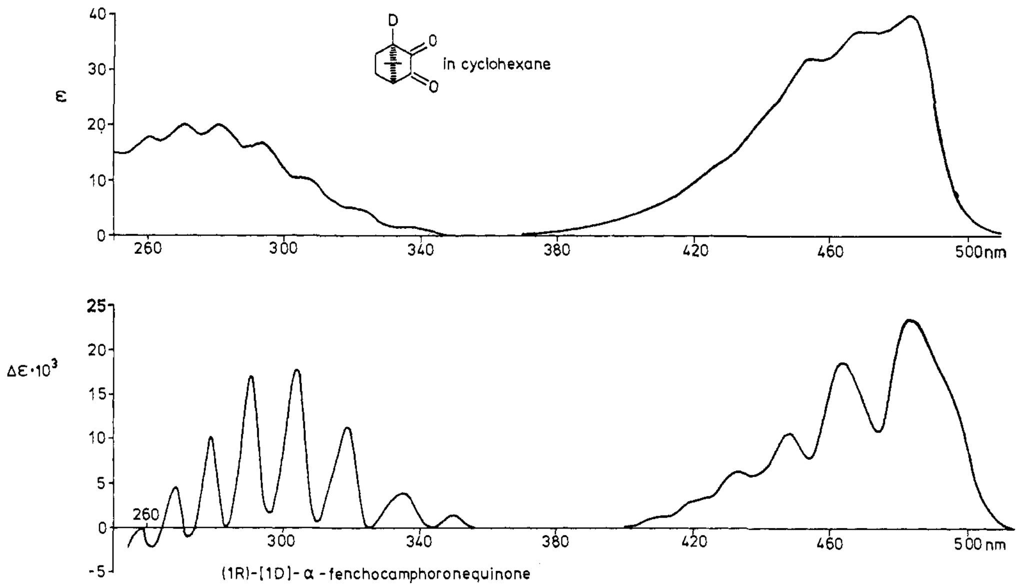

Figure 1.

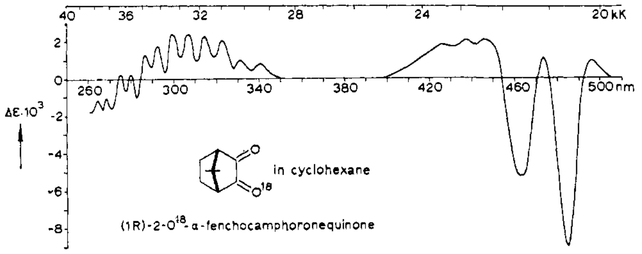

Figure 2.

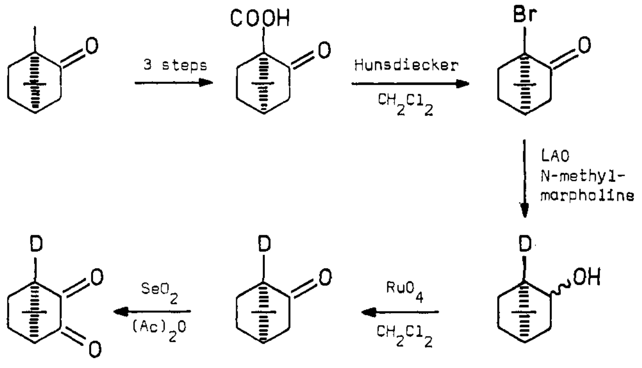

Figure 3.

interest to study related diones with optical activity due to isotopic substitution.

In this communication we report the CD spectrum of (1*R*)-[1-^{2}H]-α-fenchocamphoronequinone (II) (Figure 1). This is the first example of a CD curve of a compound whose chirality is due only to deuterium substitution. For comparison the CD spectrum of I (Figure 2) is also given.[2,3]

For the explanation of these CD curves (Figures 1 and 2), which has a direct bearing on the theory of the electronic and geometrical structure of α-diketones, several possibilities may be thought of. One may consider the mixing of symmetric and antisymmetric vibrational modes due to asymmetric distribution of mass. One may also consider the influence of isotopes on the shape of a molecule *via* anharmonicity of potential curves (change in equilibrium bond lengths and bond angles). In the case of double minimum curves (twisted α-dicarbonyl group, *e.g.*) a consideration of a possible shift in equilibrium between conformers may be appropriate.

This last point is not far-fetched because it is known that small bicyclic molecules are not necessarily rigid, but may exist in conformers as has been established beyond doubt in the bicyclo[2.2.2]octane series.[4] Valence force calculations[5] indicated that conformational equilibria might also occur in the norbornane series. In this context it is noteworthy that the CD spectrum of II in the visible region in 2-MeTHF did not show a measurable change on lowering of the temperature to −110°. At room temperature the CD of II in acetonitrile was about the same as in cyclohexane. It is therefore very unlikely that the observed CD of II should be ascribed to a shift in a conformational equilibrium due to introduction of deuterium.

Details of the synthesis of II will be published separately by one of the authors (Kokke). A scheme of the route followed by him[6] is given in Figure 3.

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(2) These spectra have been corrected to optical and isotopic purity.

(3) We estimate the error of the $\Delta\epsilon_{max}$ values in the two absorption bands of II to be less than 2%. The accuracy is going down with decreasing Δε; the error in the values of Δε in the absorption band of I around 290 nm can be as high as 15%. These inaccuracies are determined mainly by the signal-to-noise ratio and, to a lesser extent, also by a drift of the base line during the measurement.

(4) O. Ermer and J. D. Dunitz, *Helv. Chim. Acta*, **52**, 1861 (1969); E. Hirota, *J. Mol. Spectrosc.*, **38**, 367 (1971).

(5) C. Altona and M. Sundaralingam, *J. Amer. Chem. Soc.*, **92**, 1995 (1970).

(6) The observed CD curve (Figure 1) is not due to some spurious impurity because undeuterated α-fenchocamphoronequinone, prepared from the precursor 1-bromo-7,7-dimethylnorcamphor following the same route (Figure 3), was optically inactive (no effect in CD), and repeated recrystallization of II did not influence its CD.

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