

Direct Observation of Enantiomeric Rotational Isomers using ^1H Nuclear Magnetic Resonance Spectroscopy

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Summary The existence of enantiomeric rotational isomers in solutions of certain 5-oxidovinylphenanthridiniums and other sterically hindered molecules has been demonstrated by ^1H n.m.r. spectroscopy using tris-[3-(trifluoromethylhydroxymethylene)-(+) -camphorato]europium(III).

A RECENTLY reported^{1,2} variable temperature ^1H n.m.r. study of certain 5-oxidovinylphenanthridiniums showed that their 5- and 6-substituents were immobilized on the n.m.r. time-scale at 34°. For (1) this gives two (\pm) pairs

of diastereoisomeric rotamers [*e.g.* (1a), (1b)] and the ^1H n.m.r. spectrum shows six resonances due to the *Me* and *OMe* groups. In the presence of tris-[3-trifluoromethylhydroxymethylene-(+) -camphorato]europium(III) (9)³ each of the four species present gives rise to a distinct set of methyl resonances and twelve lines are observed in this region of the spectrum. These lines comprise two unequal sets in the ratio 65:35 due to the diastereoisomers, each subdivided into pairs of equal intensity due to the racemic composition of these diastereoisomers.

Compounds (2)—(4) showed¹ no diastereoisomeric peak

TABLE. Proton resonances

Compound	Partial spectrum (60MHz; τ -values; J in Hz) for CDCl ₃ solutions	Moles (9) per mole compound	Partial shifted spectrum in presence of (9)
(1)	ArMe (3H) 7.82 (34%), 8.03 (66%) OMe (3H) 6.20 (66%), 6.26 (34%) OMe (3H) 6.46 (34%), 6.59 (66%)	0.40	ArMe (3H) 6.45 (16%), 6.69 (16%), 7.28 (35%), 7.33 (33%) OMe (3H) 5.20 (30%), 5.33 (31%), 5.60 (20%), 5.63 (19%) OMe (3H) 5.75 (17%), 5.80 (18%), 5.90 (34%), 5.93 (31%)
(2)	OMe (3H) 6.70	0.48	OMe (3H) 7.27 (49%), 7.35 (51%)
(3)	OMe (3H) 6.21 OMe (3H) 6.52	0.94	OMe (3H) 5.41 (53%), 5.44 (47%) OMe (3H) 5.60 (52%), 5.67 (48%)
(4)	vinyl-H (1H) 0.62	0.50	vinyl-H (1H) 0.39 (48%), 0.52 (52%)
(5)	CH ₂ CH ₂ (2H) 5.55 6-Me (3H) 6.73	0.17	CH ₂ CH ₂ (2H) 5.14 (50%), 5.18 (50%) 6-Me (3H) 6.43 (50%), 6.52 (50%)
(6)	2'-CO ₂ Me (3H) 6.02	0.50	2'-CO ₂ Me (3H) 4.59 (49%), 4.73 (51%)
(7)	ArCH ₂ (2H) 4.73 d (J 15) (50%), 4.99 d (J 15) (50%)	0.30	ArCH ₂ (2H) 3.87 d (J 15) (50%), 4.57 d (J 15) (25%), 4.73 d (J 15) (25%)
(8)	OMe (3H) 6.01 OMe (3H) 6.81 OMe (3H) 6.40	0.60	OMe (3H) 5.38 (51%), 5.43 (49%) OMe (3H) 6.17 (52%), 6.20 (48%) OMe (3H) 5.31 (51%), 5.39 (49%)
single rotamer	CHMe (3H) 7.83 d (J 7)		CHMe (3H) 7.18 (50%), 7.28 (50%)
(10)	ArMe (3H) 7.87	0.09	ArMe (3H) 7.43 (48%), 7.60 (52%)
(11)	ArMe (3H) 7.95	0.06	ArMe (3H) 7.67 (50%), 7.77 (50%)
(12)	ArCH ₂ (2H) 4.62 d (J 14) (50%), 6.49 d (J 14) (50%) CH ₃ (3H) 8.92 t (J 7)	0.36	ArCH ₂ (2H) 0.13 d (J 14) (26%), 0.20 d (J 14) (23%) 4.37 d (J 14) (51%) CH ₃ (3H) 7.70 t (J 7) (49%), 7.93 t (J 7) (51%)

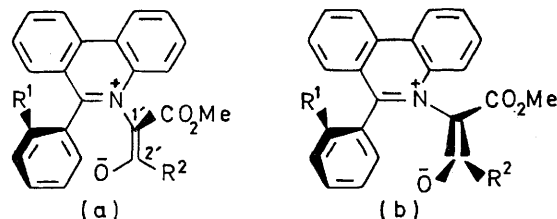
doubling in their unshifted n.m.r. spectra since the 6-phenyl substituent has an axis of symmetry along the bond joining it to the phenanthridine ring and the presence of enantiomeric rotamers could only be inferred from the behaviour of (1) and in other indirect ways. Compound (2) in the presence of (9) (0.48 mol) showed two equally intense methoxy-signals which constitute direct evidence for the racemic composition of (2) in solution, and by implication for the existence of hindered rotation. The lifetime of the enantiomers must be longer than the n.m.r. transition time and longer than the lifetime of the (2)—(9) complex. Compound (3) gave rise to four nearly equal methoxy-peaks, demonstrating the presence of equal amounts of enantiomers. The CO₂Me resonance for (4) was not doubled by (9), but the vinyl proton signal divided into two equal resonances (Δ 0.13 p.p.m.).

The 6-alkyl analogues (5) and (6), not formerly suspected⁴ to show hindered rotation, behaved in the same way as the 6-aryl compounds. The 6-methyl resonance and one of the ester methylene quartets of (5), and the 2'-CO₂Me signal of (6) doubled in the presence of (9).

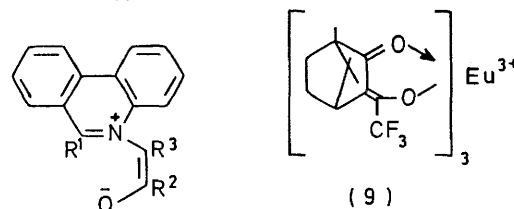
The 6-aryl compounds (7) and (8) were considered² on the basis of their n.m.r. spectra to exist in solution as rotamers, and the diastereoisomers of (8) were separated. For (7), progressive addition of (9) led first to the resolution of the benzylic methylene AB quartet into two AM systems, and then to the appearance of four equal methoxy-signals, while for the one diastereoisomer of (8) examined the 2'-CO₂Me and CHMe resonances each divided into two.

In all the compounds (1)—(8) lanthanide co-ordination is considered to occur at the vinyl oxygen by analogy with the known¹ preference of other electrophiles (H⁺, MeI/AgBF₄, PCl₃, BF₃) for this site.

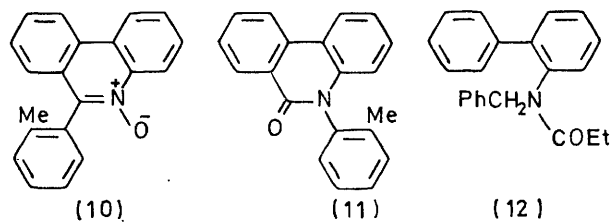
The technique has been applied to other classes of compound suspected to exist in racemic form through hindered rotation. The oxide (10) showed two equal aromatic methyl resonances in the presence of (9) corresponding to the presence of the enantiomeric rotamers, although the less nucleophilic and less hindered 6-*o*-tolylphenanthridine gave no corresponding effect. The isomeric amide (11) was



- (1) R¹ = Me, R² = CO₂Me
 (2) R¹ = H, R² = Ph
 (3) R¹ = H, R² = CO₂Me
 (4) R¹ = R² = H



- (5) R¹ = Me, R² = R³ = CO₂Et
 (6) R¹ = Et, R² = R³ = CO₂Me
 (7) R¹ = PhCH₂, R² = R³ = CO₂Me
 (8) R¹ = PhCHMe, R² = R³ = CO₂Me



strongly nucleophilic towards (9), consistent⁶ with the enhanced oxygen basicity characteristic of amide carbonyl

groups, and its methyl resonance appeared as two equally intense singlets which persisted at 93° in tetrachloroethylene.

In the presence of (9), another amide (12) known⁵ to exhibit hindered rotation from its unshifted n.m.r. spectra at various temperatures, showed two equally intense AX systems and triplets for the benzylic methylene and methyl protons, respectively. It is concluded that the hindered

rotation about the Ar-N bond leads to these enantiomeric rotamers.

Compound (9) therefore provides a new approach to the n.m.r. investigation of hindered rotation.

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