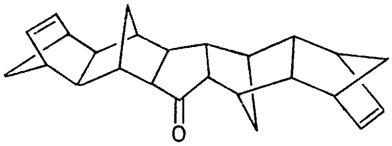
Resolution, Spectra, Dipole Strength, and Rotational Strength of (+)-(1*S*,5*S*)-Bicyclo[3.2.0]heptan-3-one

By Jan C. A. Windhorst

(*Gorlaeus Laboratories, The University of Leiden, P.O. Box 75, Leiden, The Netherlands*)

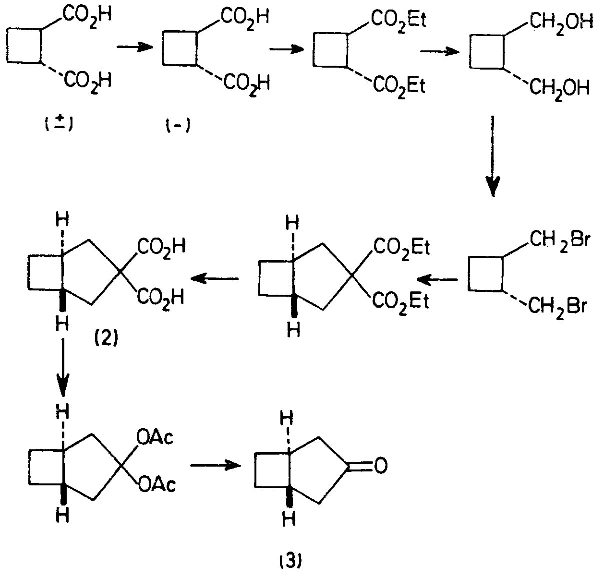
Summary Enantiomerically pure (+)-(1*S*,5*S*)-bicyclo-[3·2·0]heptan-3-one has been prepared and characterized, and its c.d. spectra, rotational strength, and dipole strength have been determined; its rotational strength is unusually large.

Recently Weissberger[1] reported the exceptional rotatory power of the dissymmetric cyclopentanone (**1**), but since its u.v. and c.d. spectra were recorded in different solvents values for its rotational strength (R.S.) and dipole strength (D.S.) cannot be compared. We have prepared (**3**), another dissymmetric cyclopentanone, from (−)-(1*R*,2*R*)-cyclobutane-1,2-dicarboxylic acid,[2,3] according to the procedure for racemic (**3**),[4,5] *via* (−)-(1*S*,5*S*)-bicyclo-[3.2.0]heptane-3,3-dicarboxylic acid (**2**) (Scheme). Crude (**3**) was purified by preparative g.l.c. (Varian A 90, OV 210, T_c 110 °C)[3] and characterized by i.r., u.v., c.d. ^{1}H n.m.r. and mass spectroscopy, and comparison with data for



(1)

racemic (3).[4] The absolute configuration of (3) was established by applying the octant rule,[3,6] V.F.F.–R.S. calculations,[3,7] and by comparison with homologous



Scheme

dissymmetric bicyclic cyclopentanones,[3] all three methods giving the same result. The enantiomeric purity of (3), determined by circular polarization of luminescence[3,8] was *ca.* 100%. U.v. and c.d. spectra were recorded in iso-octane at room temperature with a spectral resolution of 1 nm (Figure).

Pure (3) showed: $[\alpha]_D + 568°$, $[\phi]_D + 625°$, (c 0·333, iso-octane); u.v. λ_{max} (iso-octane): 290, 300, 311, and 323 nm (ϵ: 41·51, 52·65, 48·29, and 24·70, respectively); c.d. λ_{max} (iso-octane): 290, 300, 311, and 323 nm ($\Delta\epsilon$: 6·87, 9·73, 9·87, and 5·31, respectively); ^1H n.m.r. $\delta[(CD_3)_2SO]$ 0·49–2·10 (m); i.r. (neat) ν_{max} 1743s cm^{-1} (C=O); m/e 110; D.S. $6·5 \times 10^{-51}$ (S.I. units);† R.S. = $22·0 \times 10^{-53}$ (S.I. units).†‡ Although Weissberger does not give a value for the R.S. of (1) we estimate it to be *ca.* 6—7 × 10^{-52} S.I. units from its c.d. spectrum. The R.S. value for (3) is unusually large for a saturated ketone; the absolute value for the R.S. of (—)-(1*R*,6*R*)-bicyclo[4.3.0]nonan-8-one is $17·0 \times 10^{-53}$ S.I. units.[4]

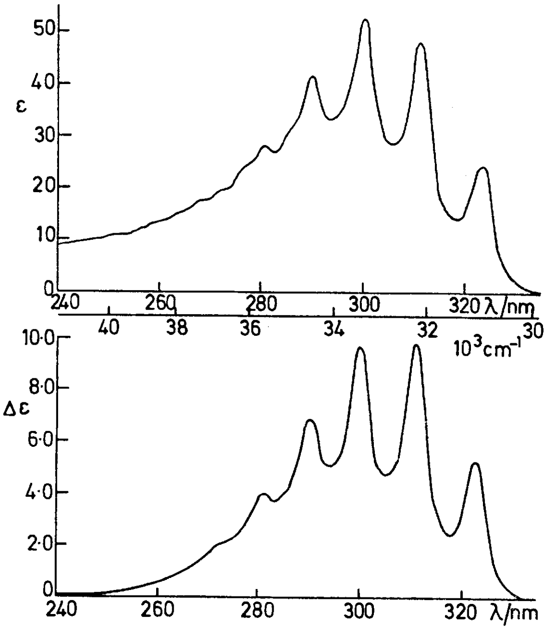


Figure C.d. spectra of (3).

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† The experimental values for R.S. and D.S. were obtained from the u.v. and c.d. spectra where ε and Δε were plotted as functions of ln $\bar{\nu}$, and the area under the curve determined; *cf.* also S. F. Mason, *Quart. Rev.*, 1963, **17**, 20.

‡ The dissymmetry factor is small enough $[g_{max}(\lambda) = 0·22]$ to neglect deviations from the Bouguer–Lambert–Beer law; *cf.* also F. Woldbye and S. Bagger, *Acta Chem. Scand.*, 1966, **20**, 1145.

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[7] We used valence force field calculations to compute the geometry of (3), and this computed geometry was used in the R.S. calculation (*cf.* also: ref. 3; and C. Altona and H. Faber, *Fortschr. Chem. Forsch.*, 1974, **1**, 45 and references cited therein).

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