(S)-(−)-Spiro(4,4)nonane-1,6-dione, X-Ray Analysis and Valence-force Calculations

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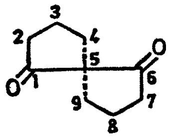
Summary The crystallographically related five-membered rings in chiral spiro(4,4)nonane-1,6-dione adopt a conformation intermediate between envelope and half-chair form but closer to the latter; the angle between the two C=O vectors is 84°.

THE preparation of optically pure laevorotary spiro(4,4)-nonane-1,6-dione (1) was first reported by Gerlach.[1] On the basis of a Horeau analysis[2] the 5*S* configuration was assigned to (1.)

In addition to the unusual spectral properties (i.r. and u.v.) of the racemic diketone,[3] compound (1) showed a surprising number of peaks in its c.d. curve.[1] The availability of a sound model is a prerequisite for the inter-



pretation of these findings. Although the nearest-neighbour spatial surroundings of the keto-groups in (1) formally resemble those in 17-keto-steroids, the pseudorotational properties[4] of the five-membered rings of (1) and of steroid ring D are different. In fact, *a priori* guessing the geometry seemed in this case a dangerous procedure.

We now report preliminary results of an *X*-ray analysis of (1) and, in addition, the geometry of the "free" molecule calculated by means of valence-force (VF) energy minimizations.[5] The latter method has proved to be a powerful tool for the study of ring D in 17-keto-steroids[4] but its applicability to spiro-compounds remained untested.

Crystal data: Orthorhombic, space group $P2_12_12$, D_2^3, $a = 8{\cdot}377$, $b = 8{\cdot}633$, $c = 5{\cdot}600$ Å at −160°; the unit cell contains two molecules of (1), the asymmetric unit comprises one half molecule. The two halves are related by the two-fold axis along *c*. A total of 997 reflexions was collected at −160° on an automatic three-circle diffractometer, employing the θ–2θ scan mode and Mo-K_α radiation. The structure was found from a three-dimensional Patterson synthesis. The least-squares analysis proceeded satisfactorily; at the present stage $R = 0{\cdot}077$, the e.s.d. of the individual non-hydrogen atomic positional parameters is of the order of 0·005 Å. The observed geometry, atomic numbering, and thermal vibration ellipsoids are shown in Figure 1a, the calculated VF geometry in Figure 1b.‡ Most of the geometrical details of the observed structure are reproduced by the calculations, within the limits of error of the observations.[5] Noteworthy exceptions are the bond angles C(5)–C(1)–O and C(2)–C(1)–O which differ by +3° and −4°, respectively, from the observed angles.

Of particular interest are the endocyclic torsion angles which reveal that the conformation of each five-membered ring is "in between" the C_s [envelope form, mirror plane through C(3)] and C_2 [half-chair form, two-fold axis through C(1)] geometries, though clearly tending toward the latter. A quantitative description can be given, using the Δ-ϕ_m notation introduced earlier[4,7] to describe the exact "point" on the pseudorotational itinerary of five-membered rings. By definition and convention we have: $\Delta(C_2) = 0°$, $\Delta(C_s) = \pm 36°$.§ For (1) we find: Δ(obs) = 9·7°, Δ(VF) = 5·3°, ϕ_m(obs) = 38·9°, ϕ_m(VF) = 38·6°. A true-to-scale octant projection of (1) is shown in Figure 2. The observed angle between the C=O vectors is 84° (VF: 72°), the distance between their midpoints is 2·88 Å (VF: 2·79 Å).

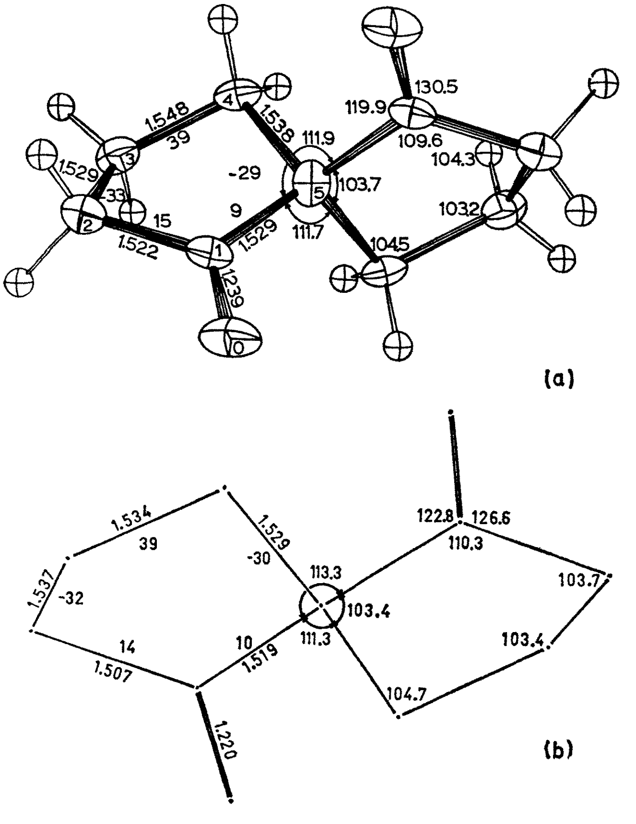


FIGURE 1 (a). *ORTEP-projection*[6] *of the molecule down the* c *axis, the thermal ellipsoids of the non-hydrogen atoms are scaled to enclose 75% probability.*

(b). *Calculated geometry, not on true scale.*

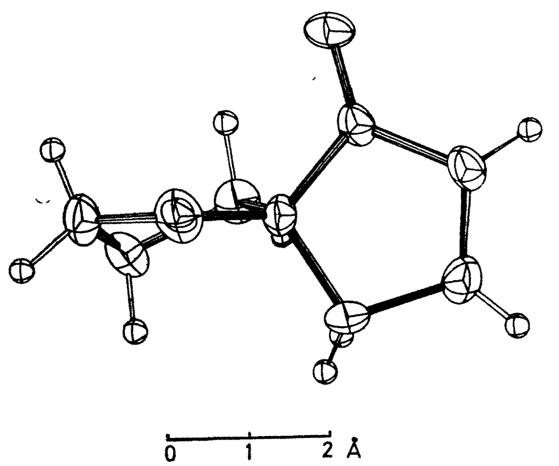


FIGURE 2. *Octant projection along the* O=C(1) *vector. Thermal ellipsoids are scaled to enclose 75% probability.*

The anisotropic vibrational amplitudes of the ring atoms are rather small with the major axes directed approximately *in* the plane of the five-membered rings, suggesting that they are better described in terms of rigid-body vibrations rather than non-rigid up and down motions which would result from large pseudovibrational freedom.[4] One has no proof that the geometry observed in the crystal is maintained in solution but the close correspondence between the *X*-ray and the VF results as well as the lack of detectable pseudolibration make it plausible that this is indeed the case.

‡ A list of observed and calculated atomic positions is available on request from the authors. The VF calculations were carried out with the same programs and force-field as reported previously.[5]

§ Δ is called the phase angle of pseudorotation, ϕ_m stands for the largest torsion angle ϕ of the ring at the $\Delta = 0°$ point (see refs. 7 and 4 for a discussion of the interrelationship between the five torsion angles in the cyclopentane ring). In the present case the value of Δ(obs), 9·7°, is rather closer to 0° (C_2) than to +36°(C_s).

The Figures show the "correct" stereochemistry of the molecule[1] but this assignment of absolute configuration has not yet been confirmed by X-ray methods. We hope to carry out the necessary experiments in the near future.

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[1] H. Gerlach, *Helv. Chim. Acta*, 1968, **51**, 1587.
[2] A. Horeau, *Tetrahedron Letters*, 1961, 506.
[3] D. J. Cram and H. Steinberg, *J. Amer. Chem. Soc.*, 1954, **76**, 2753.
[4] C. Altona, "Conformational Analysis", Academic Press, New York, 1971, p. 1, and refs. therein.
[5] C. Altona and M. Sundaralingam, *J. Amer. Chem. Soc.*, 1970, **92**, 1995; *Tetrahedron*, 1970, **26**, 925.
[6] C. K. Johnson, *Chem. Div. Ann. Prog. Rept. Oak Ridge Natl. Lab.*-4164, 1967, 116.
[7] C. Altona, H. Geise, and C. Romers, *Tetrahedron*, 1968, **24**, 13.