A Very Long Carbon–Carbon Bond in a Cyclopropane Derivative

By RICCARDO BIANCHI, ANGELO MUGNOLI, and MASSIMO SIMONETTA*
(*Istituto di Chimica Fisica dell'Università e Centro C.N.R., Via Saldini* 50, 20133 *Milano, Italy*)

Summary An *X*-ray crystal structure determination of 11,11-dimethyltricyclo[4,4,1,$0^{1,6}$]undeca-2,4,7,9-tetraene shows a C(1)–C(6) bond distance of *ca.* 1·80 Å; the molecular geometry corresponds to a non-aromatic compound with a bisnorcaradiene structure.

FOLLOWING our interest in the geometry of bridged annulenes,[1–4] we undertook the crystal structure determination of the undecatetraene (1). N.m.r. results[5] had suggested the presence of a direct bond between C(1) and C(6) in a bisnorcaradiene structure.

The substance (m.p. 88°) decomposes rapidly in air; for the *X*-ray analysis crystals sealed in Lindemann glass were used. The compound, $C_{13}H_{14}$, crystallizes in the triclinic system, space group $P1$, with $a = 8{\cdot}089$, $b = 7{\cdot}007$, $c = 9{\cdot}886$ Å, $\alpha = 100{\cdot}47$, $\beta = 95{\cdot}91$, $\gamma = 115{\cdot}46°$, $Z = 2$, $D_m = 1{\cdot}157$, $D_c = 1{\cdot}161$ g cm^{-3}. Measurements were made over nearly all Cu-K_α hemisphere using a linear diffractometer with Mo-K_α radiation and a silicon monochromator. The $N(z)$ test was in full agreement with the non-centric distribution.


(1)

The orientations of the two molecules of the asymmetric unit with respect to the crystal axes were obtained by angular scanning of the three-dimensional Patterson synthesis, considering maximum overlap with vectors

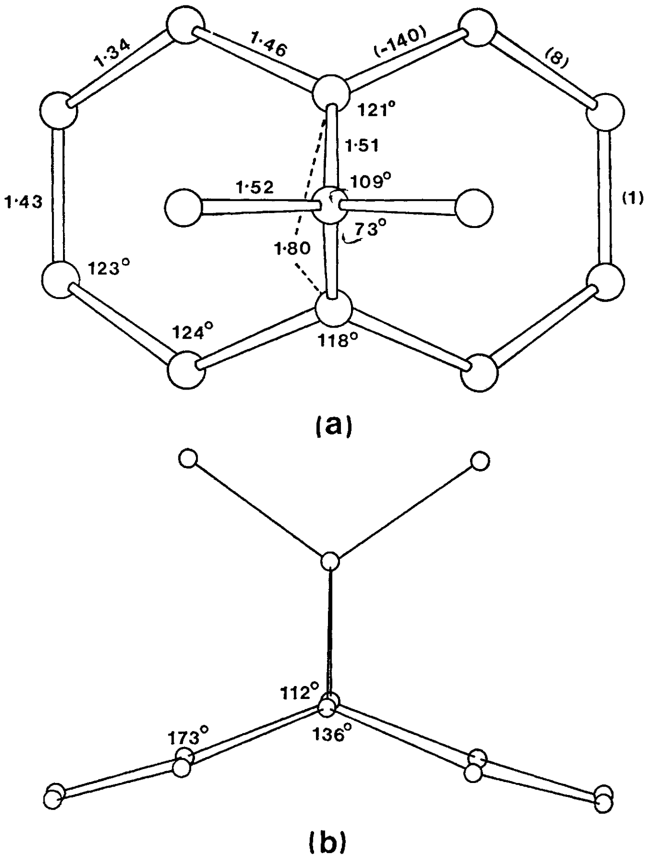

FIGURE. *One molecule of* (1) *viewed along two principal axes of inertia.* mm2-*averaged geometric parameters are reported.* (a) *Bond lengths, angles, and* (*in parentheses*) *torsion angles*; (b) *Dihedral angles.*

relative to an assumed molecular model.[6] The first (orientated) molecular model was then fixed at the origin, and the position of the second (orientated) molecule with respect to the first was determined by the minimum residual technique, by shifting the model along the *x*, *y*, and *z* axes.[7] Anisotropic least-squares refinement is in progress; the current *R* index over about 1800 reflexions is 0·067.

In both molecules the geometry is clearly non-aromatic (in contrast to that of the related compound[2] with fluorine instead of methyl groups). Here the configuration is of the bisnorcaradiene type, and the central distance C(1)–C(6) corresponds to a long bond which closes the cyclopropane ring [C(1), C(6), and C(11)]. Some chemically equivalent molecular parameters are significantly different in the two molecules of the asymmetric unit; the highest discrepancies are found for the C(1)–C(6) distances (1·82 and 1·77 Å respectively, σ 0·01 Å) and the C(1)–C(11)–C(6) bond angles (74·5 and 71·7° respectively, σ 0·5°). Because there are two independent molecules in different environments, and because the C(1)–C(6) bond is long and therefore weak, packing forces might account for the observed differences in the two C(1)–C(6) lengths.

The geometry of the perimeter ring, and the C(1)–C(6) distance which can be considered as corresponding to a very long C–C single bond, support previous n.m.r. results[5] and confirm the bisnorcaradiene structure.

The molecular symmetry is nearly *mm*2 (C_{2v}); within the same molecule the maximum deviations are 0·025 Å, 1·5°, and 3·5° in bond lengths, bond angles, and absolute values of torsion angles respectively. The Figure summarizes the geometric parameters, averaged over the two molecules by assuming *mm*2 symmetry.

We thank Professor E. Vogel for the crystals, and Professor K. Dornberger-Schiff and Dr. C. M. Gramaccioli for discussions.

(*Received*, 26*th June* 1972; *Com.* 1103.)

---

[1] G. Casalone, A. Gavezzotti, A. Mugnoli, and M. Simonetta, *Angew. Chem. Internat. Edn.*, 1970, **9**, 519; A. Gavezzotti, A. Mugnoli, M. Raimondi, and M. Simonetta, *J. C. S. Perkin II*, 1972, 425.

[2] C. M. Gramaccioli and M. Simonetta, *Acta Cryst.*, 1971, B **27**, 2231.

[3] C. M. Gramaccioli, A. Mimun, A. Mugnoli, and M. Simonetta, *Chem. Comm.*, 1971, 796.

[4] C. M. Gramaccioli, A. Mugnoli, T. Pilati, M. Raimondi, and M. Simonetta, *Chem. Comm.*, 1971, 973; *Acta Cryst.*, 1972, **B28**, 2365.

[5] E. Vogel, *Pure and Appl. Chem.*, 1969, **20**, 237.

[6] G. Filippini and C. M. Gramaccioli, *Ricerca Sci.*, 1969, **39**, 589. The FORTRAN IV program was extended to the triclinic case by one of us (R.B.).

[7] FORTRAN IV program written by C. M. Gramaccioli.