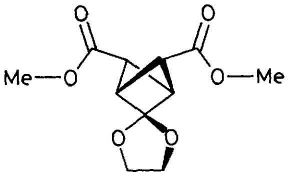
Electron Density Distribution in the Bonds and Nonbonded Contacts of a Bicyclo[1.1.1]pentane Derivative

Hermann Irngartinger,*[a] Wolfgang Reimann,[a] Paul Dowd,[b] and Philip Garner[b]

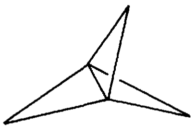
[a] *Organisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-6900 Heidelberg 1, F.R.G.*
[b] *Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, U.S.A.*

The difference electron density along the very short C···C contact (1.9226 Å) of the bicyclo[1.1.1]pentane (**1**) determined by low-temperature (100 K) *X*-ray structure analysis is negative, and comparison is made with the [1.1.1]propellane system recently published; the bicyclo[1.1.1]pentane bonds are bent by about 10°.

Having elucidated the structures of the *exo,exo*-bicyclo-[1.1.1]pentane diester (**1**) and its *exo,endo*- and *endo,endo*-isomers[1] we determined the electron density distribution in the bonds and the short nonbonded contacts of (**1**) by



(**1**)



(**2**)

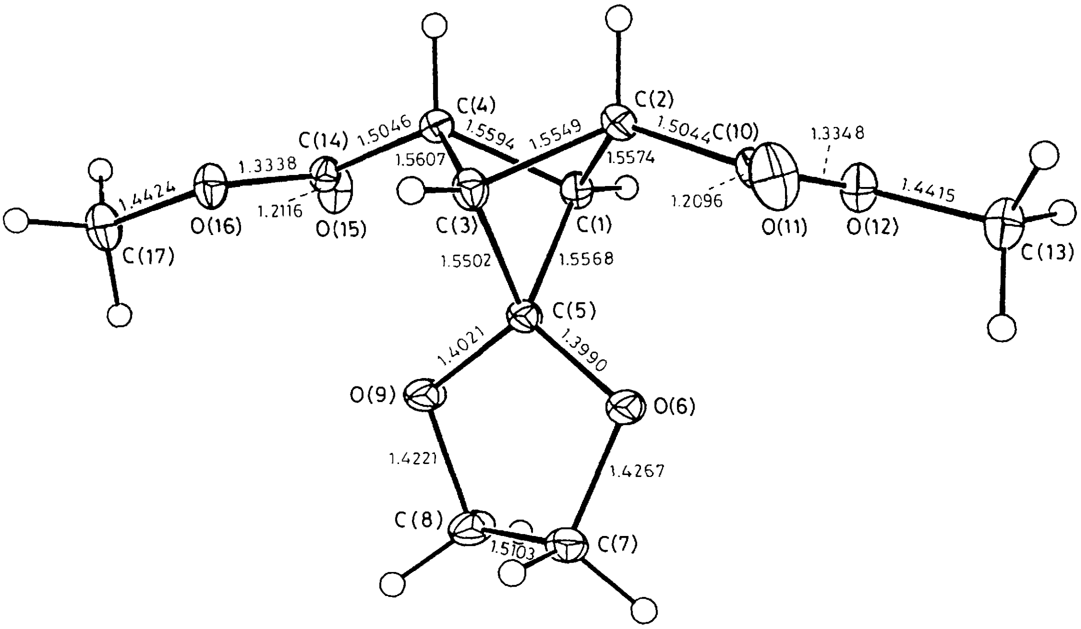


Figure 1. Structure of (**1**) and bond lengths (Å) at 100 K. Standard deviations 0.0006—0.0008 Å.

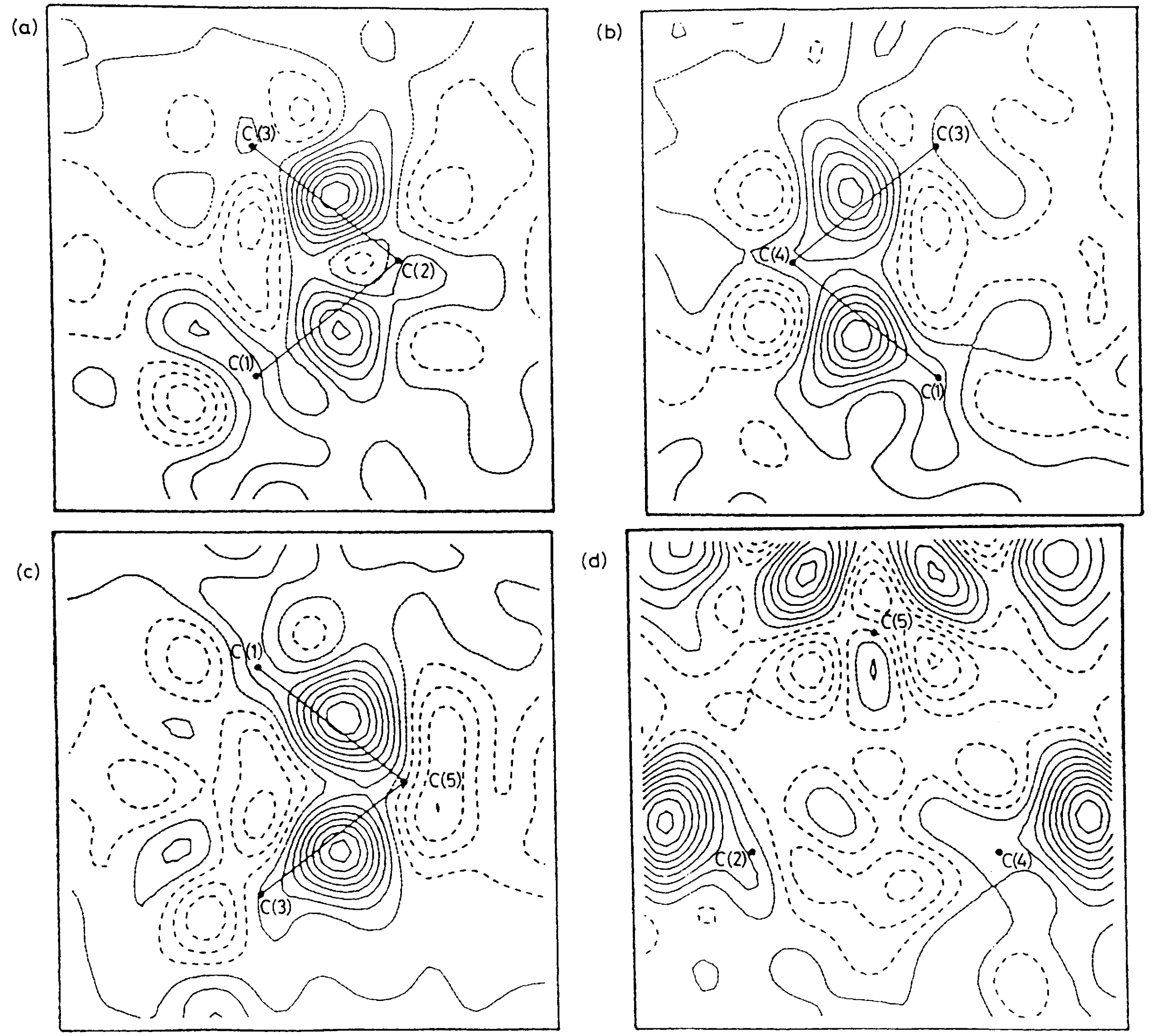


Figure 2. Difference density sections along the C(1) $\cdots$ C(3) contact in the planes of the atoms (a) C(1), C(2), C(3); (b) C(1), C(3), C(4); (c) C(1), C(3), C(5) and perpendicular to this contact in the plane of the atoms; (d) C(2), C(4), C(5). The contour intervals are 0.05 e Å^{-3}. The zero line is dotted, negative regions have dashed lines. The averaged standard deviation in the area away from the atomic positions is 0.02 e Å^{-3}.

low-temperature X-ray diffraction at 100 K[†] with the X–X method.[2] Among organic molecules the bicyclo[1.1.1]pentane system has the shortest nonbonded $C \cdots C$ contact [(**1**) : C(1) $\cdots$ C(3) 1.9226(7) Å; Figure 1; other derivatives (X-ray at room temperature) have distances in the range 1.856—1.907 Å[1,3]]. Large NMR coupling constants arise from this contact,[4,5] and back-lobe interactions have been discussed in this connection.[5] These arguments and the comparison with

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[†] *Crystal data* for (**1**) at 100 K: A suitable crystal with the dimensions 0.4 × 0.4 × 0.45 mm was selected. Cell dimensions were determined by least-squares method from 40 high-order reflections: a = 18.437(2), b = 8.541(1), c = 14.019(2) Å; orthorhombic, space group $Pbca$; Z = 8; D_c = 1.44 Mg/m^3; five independent data sets have been collected up to sin θ/λ = 0.66 and 2.5 independent sets in the range 0.66<sin θ/λ < 1.2 Å^{-1}, with a total number of 28000 reflections. Absorption corrections were applied and the intensities were averaged (R_{Int} = 0.02). Enraf-Nonius CAD4 diffractometer, Mo-K_α radiation, graphite monochromator: sin θ/λ <0.7 Å^{-1}: 3004 observed reflections [I>2.65 $\sigma(I)$] for calculation of the difference densities; sin θ/λ = 0.7—1.2 Å^{-1}: 2857 observed reflections for the refinement with the reflections of high order (C,O anisotropic, full matrix); R = 0.033; 1539 'unobserved' reflections [I<2.65$\sigma(I)$] were included in the refinement. The positional and the isotropic thermal parameters of the H atoms have been determined within the low order refinement (sinθ/λ <0.7 Å^{-1}; R = 0.035). According to the 'rigid bond test',[11] the difference of the thermal vibration contribution of two atoms along the bond connecting both atoms should be smaller than 0.001 Å^2. The maximum difference for this structure is 0.0006 Å^2; the average value is 0.0004 Å^2. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

the [1.1.1]propellane system (**2**) aroused our interest in the electron density distribution along the short contact. Although the 1,3-bonding distance in the [1.1.1]propellane system (1.577—1.60 Å)[6] is shorter than the nonbonding contact in the bicyclo[1.1.1]pentanes, no difference electron density has been detected in the bonding region of [1.1.1]propellane systems.[6a]

In the three sections along the C(1) ··· C(3) contact of (**1**) and in the section perpendicular to this contact only negative electron density contributions (-0.15 e Å^{-3}) are found (Figure 2). This is in agreement with recent calculations[7] which examined the Laplacian, the second derivative of the electron density, and which found no bond between C(1) and C (3) in bicyclo[1.1.1]pentane. For (**2**) such calculations do show bonding properties along C(1)–C(3).[7] Theoretical results[8,9] at variance with these calculations are explained[7] by the fact that only subsets of orbitals are considered for total properties. The negative electron density in the central bond of (**2**) is interpreted by resolution problems,[6a] by inverted geometries at the bridgehead carbon atoms, and by differences between the spherical atom reference state and the valence state.[6a,7]

The electron density maxima on the C–C bonds (mean bond length 1.557 Å) of the bicyclo[1.1.1]pentane skeleton of (**1**) are shifted outwards by 0.1 Å on average from the internuclear connection lines [Figure 2(a—c)] demonstrating clearly bent bonds in these highly strained polycyclic systems. The angles between the lines from the atoms C(2), C(4), or C(5) to the neighbouring density maxima are larger by about 20° than the corresponding bond angles (76.3°). The corresponding angles for the bent bonds of bicyclo[1.1.1]pentane from quantum mechanical calculations range from 10 to 30°.[7,10]

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