JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 8, 94–96 (1995)

A REMARKABLY BENT ALLENE. X-RAY CRYSTAL STRUCTURE AND *AB INITIO* CALCULATIONS

EDWIN WEBER* WILHELM SEICHTER
Institut für Organische Chemie, Technische Universität Bergakademie Freiberg, Leipziger Strasse 29, D-09596 Freiberg/Sachsen, Germany

BERND HESS
Institut für Physikalische und Theoretische Chemie der Universität Bonn, Wegelerstrasse 2, D-53115 Bonn, Germany

AND

GEORG WILL AND HANS-JÜRGEN DASTING
Mineralogisch-Petrologisches Institut der Universität Bonn. Poppelsdorfer Schloss, D-53115 Bonn, Germany

X-ray data on the crystal and molecular structure of bis(biphenyl-2,2′-diyl)allene, reveal a remarkably strong deviation from linearity (170·1°) of the allene unit of the molecule. *Ab initio* calculations involving dimers of molecules yield good correlation with this geometry, showing that the non-linearity is due to packing effects in the crystal.

INTRODUCTION

In allenes, the central carbon atom is usually described as sp-hybridized.[1] Theory therefore predicts a linear geometry for cumulated double bonds that is mostly found in experiments. However, in some allenes deviations from linearity of a few degrees have also been observed.[2] Here we report an allene with an unusually large bend around the central allene carbon atom, namely bis(biphenyl-2,2′-diyl)allene (**1**).[3] This compound can easily be obtained[4] from 1,1,3,3-bis(biphenyl-2,2′-diyl)-1,2-dichloropropane by short-term heating with triethylamine in ethyl acetate (yield 15%, colourless needles[5]).

RESULTS AND DISCUSSION

The x-ray analysis of compound **1** reveals, that the allene part of the molecule shows a remarkably strong bend with a bond angle at the central carbon atom of 170·1(7)° instead of 180° (Figure 1). Also, the planes of the fluorene units are not exactly perpendicular to each other, as expected from theory, but form an angle of 85°. On the other hand, the lengths of the cumulated double bonds are 1·314 Å, which is normal.[2]

What is the reason for the anomalous bend in the molecule of crystalline **1**? Does it come from particular packing effects in the crystal, which is characterized by molecular dimers which are in turn stacked in an edge-on-plane orientation of the aromatic groups[6] of adjacent dimers (Figure 2), or is there a special electronic structure in the molecule of **1** due to the presence of the fluorene moieties?

Because some allene-analogous carbodiimides are reported to have a non-linear structure,[7,8] it seems conceivable that an electronic effect is responsible for the unusual bond angle in **1**. A possible mechanism leading to a bent geometry is the admixture of double

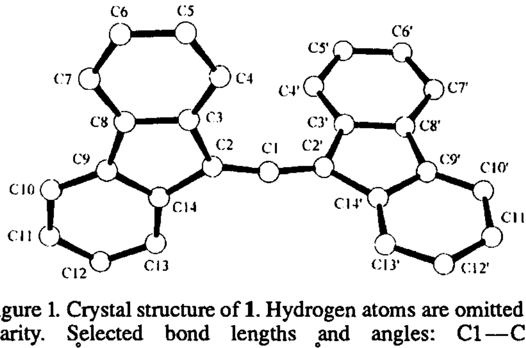

Figure 1. Crystal structure of **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles: C1—C2 = 1·314(1) Å, C2—C3 = 1·477(2) Å, C2-C14 = 1·485(2) Å, C2-C1-C2′ = 170·1(2)°, C3-C2-C14 = 105·7(1)°

---

[*] Author for correspondence.

CCC 0894–3230/95/020094–03

Received 13 June 1994
Revised 12 October 1994

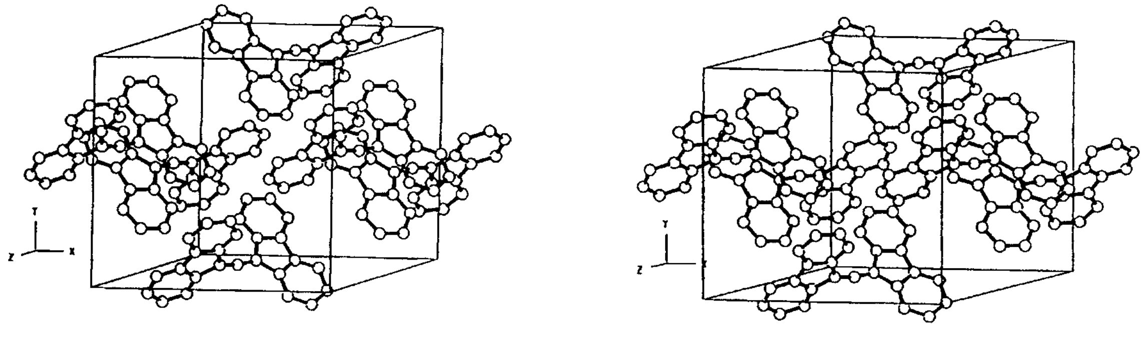

Figure 2. Stereo illustration of the packing arrangement of **1**

excitation of electrons from the highest occupied allene orbital (HOMO) to the lowest unoccupied orbital (LUMO). The latter becomes distinctly more stable if the molecule is bent, and under suitable energetic conditions, caused by substitution, this particular effect of stabilization might over-compensate destabilization of the HOMO orbital, thus giving rise to the bend. Whether such a mechanism exists depends on the details of the electron structure, which can only be solved by a calculation.

To answer this question, we carried out *ab initio* calculations using the TURBOMOLE code.[9] We calculated both the monomer **1** and its molecular dimer in a 3–21G basis set using Hartree–Fock self-consistent field (SCF) methods and Møller–Plesset second-order perturbation theory (MP2). For the molecular dimer we employed the geometry of monomers as found in the crystal and varied the bond angle of the central C-C-C group while leaving the bond distances of the respective C atoms constant. Moreover, we compared the experimental geometry (bond angle 170°) with the ideal geometry (180°) to give an energetic difference of the respective conformations designated ΔE. According to SCF calculations, ΔE of the experimental geometry of the monomer is 3·2 kJ mol^{-1} less favourable than the idealized geometry, and contributions of electron correlation level decrease this value by 0·8 kJ mol^{-1}. This corresponds with the results we have found with the semi-empirical MNDO method.[10] In this case, the experimental structure is 2·3 kJ mol^{-1} higher than the idealized structure. Considering that the MP2 method near-equilibrium distance recovers about two thirds of the correlation energy, the electronic structure of the monomer should lead to a linear arrangement of the central carbon atoms. For the unsubstituted allene, the respective energy difference is even more pronounced, amounting to about 4·8 kJ mol^{-1} (SCF, with about the same contribution for correlation). Thus, in bis(biphenyl-2,2′-diyl)allene (**1**), the bond is less rigid, but it is still linear.

Calculations of the molecular dimer reveal why the monomer is bent. Because of repulsion of π-electrons (Pauli or exchange repulsion) of the fluorene units, which are nearly parallel within the molecular dimer in the experimental geometry, the 170° configuration is stabilized by $\Delta E \approx -20$ kJ mol^{-1}. The energy versus angle plot shows a minimum at 167°. This means that the bend is caused by effects of the crystal package. The packing is thus characterized by molecular dimer units which minimize the occupied volume, which in turn leads to a distortion of the central allene angle owing to exchange repulsion. An effective attraction of the aromatic substituents is expected in an edge-on-plane arrangement, because of the interaction of the quadrupole moments of the aromatic substituents. This interaction should contribute to the cohesion across adjacent molecular dimer units.

Based on currently available theoretical methods, a reliable prediction of the crystal structure of the allene **1** cannot be made, since electron correlation plays an important role and is treated unsatisfactorily in present-day calculations of solids. Nevertheless, using calculations with periodic boundary conditions, interactions in a given crystal structure can be studied. In our case, because of the large unit cell, we applied the extended Hückel method.[11–13] This method seems to describe the interactions fairly well, since we obtained a stabilization of $\Delta E = -22$ kJ mo^{-1} for the molecular dimer in the bent conformation, which is in good agreement with *ab initio* calculations. Calculation of the solid results in a stabilization of $\Delta E = -44$ kJ mol^{-1} for the bent geometry. The energy profile shows a parabola with a minimum at the angle of 170°.

The answer to the question of why allene **1** is bent is therefore as follows. The energy recovered by crystal formation is partially compensated by the repulsive interaction of the π-electrons of the fluorene units that belong to different monomers. To reduce this interaction, a bond angle of 170° is formed, resulting in an energetic advantage of about -44 kJ mol^{-1} for the given packing density and crystal structure.

Table 1. Bond lengths with e.s.d.s in parentheses

Bond	Length (Å)	Bond	Length (Å)
C(1)—C (2)	1·314 (1)	C (7)—C (8)	1·385 (2)
C(2)—C(14)	1·485 (2)	C (8)—C (9)	1·466 (2)
C(2)—C (3)	1·477 (2)	C (9)—C(10)	1·391 (2)
C(3)—C (4)	1·382 (2)	C(10)—C(11)	1·387 (3)
C(4)—C (5)	1·392 (2)	C(11)—C(12)	1·390 (2)
C(5)—C (6)	1·378 (2)	C(12)—C(13)	1·393 (2)
C(6)—C (7)	1·390 (3)	C(13)—C(14)	1·374 (2)

Table 2. Bond angles with e.s.d's in parentheses

Bond	Angle (°)	Bond	Angle (°)
C(9')—C(14')—C(13')	121·7 (1)	C(9')—C(10')—C(11')	118·3 (1)
C(3')—C(4')—C(5')	118·6 (1)	C(10')—C(11')—C(12')	121·7 (2)
C(4')—C(5')—C(6')	120·2 (2)	C(11')—C(12')—C(13')	120·2 (2)
C(5')—C(6')—C(7')	121·2 (1)	C(12')—C(13')—C(14')	118·6 (1)
C(6')—C(7')—C(8')	118·7 (1)	C(13')—C(14')—C(9')	121·1 (1)
C(7')—C(8')—C(3')	119·7 (2)	C(9')—C(14')—C(2')	108·6 (1)
C(3')—C(8')—C(9')	108·8 (1)	C(14')—C(2')—C(3')	105·7 (1)
C(8')—C(9')—C(14')	108·5 (1)	C(2')—C(3')—C(8')	108·4 (1)
C(14')—C(9')—C(10')	120·1 (1)	C(2')—C(1)—C(2)	170·1 (2)

EXPERIMENTAL

Compound **1** was prepared according to literature procedures.[3,4] The crystal (bright yellow, octahedral, 0·20 × 0·25 × 0·25 mm) for x-ray study was grown from benzene–light petroleum.

Crystal data: $C_{27}H_{16}$, $M_r = 340{\cdot}42$, monoclinic, space group $C2/c$, $a = 13{\cdot}108(3)$, $b = 12{\cdot}487(2)$, $c = 12{\cdot}659$ Å, $\beta = 120{\cdot}67(1)°$, $V_c = 1782{\cdot}3$ Å^3, $Z = 4$, $D_c = 1{\cdot}267$ g cm^{-3}.

Nicolet P2$_1$ diffractometer (Mo $K\alpha$, graphite monochromator was used), $2\Theta_{max} = 53°$, 1982 symmetry-independent reflexes of which 1701 with $F > 3\sigma F$ were used for refinement (SHELXS 86, SHELX 76); 205 refined parameters, $R = 0{\cdot}042$, $R_w = 0{\cdot}031$. Bond lengths are given in Table 1 and bond angles in Table 2.

Supplementary data. Further details of crystal structure analysis can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich–technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany by stating the deposit number CSD-58793, authors and journal reference.

ACKNOWLEDGEMENTS

E.W. and B.H. thank the Deutsche Forschungsgemeinschaft (SFB 334) and the Fonds der Chemischen Industrie for financial support.

REFERENCES

1. S.R. Landor (Ed.), *The Chemistry of the Allenes*, Vols 1–3. Academic Press, London (1982).
2. H. Irngartinger, E. Kurda, H. Rodewald, A. Berndt, R. Bolze and K. Schlüter, *Chem. Ber.* **115**, 967 (1982).
3. E. Weber, W. Seichter and I. Goldberg, *Chem. Ber.* **123**, 811 (1990).
4. H. Fischer and H. Fischer, *Chem. Ber.* **97**, 2975 (1964).
   M. W. Haenel, H. Irngartinger and C. Krieger, *Chem. Ber.* **118**, 144 (1985).
5. Dimerization of 1 at 130 °C: E. Weber, W. Seichter, I. Goldberg, G. Will and H.-J. Dasting, *J. Incl. Phenom.* **10**, 267 (1991).
6. L. R. Hanton, C. A. Hunter and D. H. Purvis, *J. Chem. Soc.* 1134 (1992).
7. A. T. Vincent, P. J. Wheatley, *J. Chem. Soc., Perkin Trans. 2* 687 (1972).
8. H. Irngartinger, H.-U. Jäger, *Acta Crystallogr., Sect. B* **34**, 3262 (1978).
9. R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.* **162**, 165 (1989).
10. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.* **99**, 4899 (1977).
11. R. J. Hoffmann, *J. Chem. Phys.* **39**, 1397 (1963).
12. M. H. Whangbo and R. J. Hoffmann, *J. Am. Chem. Soc.* **100**, 6093 (1978).
13. R. Hoffmann, *Solids and Surfaces*. VCH, New York (1989).