X-Ray Crystal and Molecular Structure of Adamantylideneadamantane

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Summary An *X*-ray diffraction study of adamantylideneadamantane has shown that the geometry of the molecule does not show abnormal features due to steric hindrance.

ADDITION reactions involving the double bond of adamantylideneadamantane (Ad=Ad) have been described by Strating, Wieringa, and Wynberg.[1] To study the conformation around the double bond the crystal and molecular structure of adamantylideneadamantane has been determined by single crystal *X*-ray diffraction. Crystals were obtained from a solution of the compound in MeOH by evaporation of the solvent. Weissenberg photographs showed that the space group is monoclinic, $P2_1/c$. The cell dimensions, determined from Weissenberg films calibrated with NaCl spots and from the diffraction angles measured on the Nonius three-circle diffractometer, are, $a = 6{\cdot}617(7)$, $b = 10{\cdot}151(3)$, $c = 13{\cdot}314(3)$ Å and $\beta = 117{\cdot}87(2)^\circ$, $Z = 2$. As the general position in the space group is 4, the molecules have to lie on inversion centres.

For a crystal with dimensions of $0{\cdot}4 \times 0{\cdot}4 \times 0{\cdot}5$ mm^3, the intensities of 2302 reflections with $\sin \theta/\lambda > 0{\cdot}7$ Å^{-1} were measured on an automatic Nonius three-circle diffractometer with Zr-filtered Mo radiation. For 1922 reflections I(net) is non-zero. Corrections for the Lorentz and polarization effects were applied; no absorption corrections were necessary because of the small value of the absorption coefficient, $\mu = 0{\cdot}68$ cm^{-1}. The structure was found by use of the symbolic addition method.[2] An E-map calculated with 205 reflections with known signs clearly revealed the structure of the molecule. The parameters of the carbon atoms were refined by use of an anisotropic least-squares (block-diagonal) program. A difference map (H not included in F_c) revealed all the hydrogen atoms. In the refinement cycles the positions of the hydrogen atoms were kept fixed at a distance of 1·08 Å from their neighbouring carbon atoms and their isotropic temperature factors were chosen to be slightly larger than the average thermal motion of the carbon atoms. Corrections for extinction during the least-squares refinement[3] were applied and in the strongest reflection the extinction amounted to 0·27 in F. All 1922 non-zero reflections were given equal weights and $R = 0{\cdot}094$. For carbon the scattering curve of Doyle and Turner[4] was used and for hydrogen that of Stewart, Davidson, and Simpson.[5] The final co-ordinates of the heavy atoms are listed (Table) with their standard deviations as calculated by the least-squares program. All intermolecular distances in the crystal are longer than the sum of the relevant van der Waals radii.[6]

Final co-ordinates of the carbon atoms with their standard deviations as calculated by the least-squares program

Atom	10^4x	10^4y	10^4z
C(1)	183 (4)[a]	1928 (2)	−177 (2)
C(2)	284 (4)	553 (2)	308 (2)
C(3)	1094 (4)	627 (2)	1571 (2)
C(4)	−547 (5)	1488 (3)	1805 (2)
C(5)	−628 (5)	2862 (3)	1346 (2)
C(6)	1748 (5)	3483 (3)	1925 (2)
C(7)	3384 (4)	2634 (3)	1697 (2)
C(8)	2570 (5)	2552 (3)	420 (2)
C(9)	−1441 (4)	2779 (2)	68 (2)
C(10)	3486 (4)	1248 (3)	2164 (2)

[a] Standard deviations are lower estimates of the errors in the atomic co-ordinates.

The geometry of Ad=Ad has no abnormal features (see Figure). The molecule has approximately *mmm* symmetry. Except for the angles at the double bond, the valence angles are close to the tetrahedral value of 109·4°. The average values of the single bonds C(2)–C(1), C(1)–C(8), C(8)–C(7), and C(7)–C(6) are 1·517, 1·532, 1·524, and 1·524 Å, respectively. The relatively small value of the bonds of the type C(2)–C(1) may be attributed to the double bond.[7] The average length of the remaining single bonds, 1·528 Å, is equal to the value of 1·528(5) Å found for cyclohexane by gas electron diffraction.[8] The double bond and its neighbouring atoms C(1), C(3), C(1′), and C(3′) lie in a plane. The length of the double bond, 1·336(4) Å, is almost equal to the value of 1·335 Å generally accepted for double bond length.[9] The valence angles C(1′)–C(2′)–C(2) and C(3′)–C(2′)–C(2) are 124·4 and 125·3 ± 0·2°, respectively. The difference is not significant. The angle C(1)–C(2)–C(3) is 110·4 ± 0·2° These angles are not significantly different from the values observed for corresponding angles in less bulky molecules. For propylene gas a value of 124·75 ± 0·3° has been found for the C=C–C angle by microwave spectroscopy.[10] For isobutylene values of 124 and 112° have been reported for the angles C=C–C and H_3C–C–CH_3, respectively.[11] The distance of 1·90 Å between the hydrogen atoms linked to C(1) and C(3′) is appreciably shorter than the van der Waals distance[6] of 2·4 Å. It is remarkable that this short distance does not cause a significant bending of angles such as C(2)–C(1)–H. Although these angles are among the largest C–C–H angles, they are not significantly different from the average value, 109·3°, of the C–C–H angles. Therefore no apparent deformations around the double bond occur.

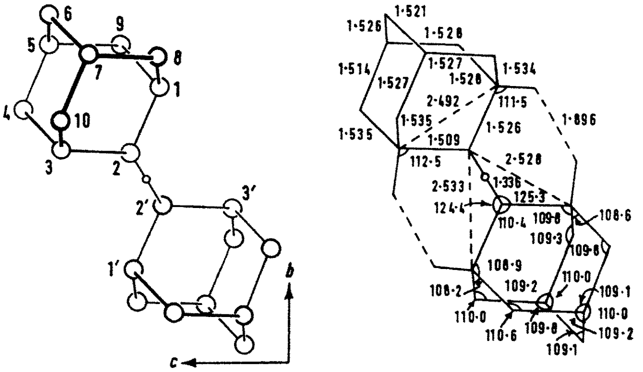

FIGURE. *A projected view of one of the molecules along the a*-axis.* The angles C(2)–C(1)–C(8) and C(2)–C(3)–C(4) are 109·1 and 109·8°, respectively.

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