A Reinvestigation of Tolane

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Abstract. $C_{14}H_{10}$, monoclinic, $P2_1/a$, $a = 12.778$ (2), $b = 5.764$ (1), $c = 15.508$ (4) Å, $\beta = 113.39$ (2)°, $Z = 4$, $R_w = 0.036$ for 1305 counter reflections. The asymmetric unit consists of two crystallographically independent half molecules with similar bond distances and angles. The molecules are planar. Semi-empirical CNDO/2 calculations predict a quasi free rotation of the phenyl ring around the C–C single bond with a rotation barrier of 0.65 kcal mol^{-1}.

Introduction. The structure of 1,2-diphenylacetylene was examined by Robertson & Woodward (1938). Their experimental data were limited to 106 reflections in the $h0l$ plane, and the results are not very accurate.

We have re-examined tolane counter data, to obtain better structural parameters.

Tolane was synthesized by a standard method (Fieser & Fieser, 1967). Crystals were obtained by cooling (24 h) a solution in methanol. A suitable crystal, $0.6 \times 0.6 \times 0.4$ mm, covered with glue to prevent sublimation, was used for data collection. The absences $h0l$: $h = 2n$, and $0k0$: $k = 2n$ and the monoclinic symmetry verified the previously reported space group (Robertson & Woodward, 1938). However, during the structure determination it was realized that the present unit cell (I) is related to that of Robertson & Woodward (II) by: $a(I) = a(II)$, $b(I) = -b(II)$, $c(I) = -[a(II) + c(II)]$. The density measured by flotation in $CaCl_2$ solution is 1.136 g cm^{-3} at 23°C and the calculated density based on four molecules per unit cell is 1.129 g cm^{-3} at 25°C.

Diffraction data were collected at an average temperature of 24.5°C with a Picker FACS-I automatic diffractometer using Zr-filtered Mo $K\alpha$ radiation ($\mu = 0.69$ cm^{-1}). The lattice parameters were obtained by least-squares refinement of the 2θ, ω, χ and φ angles of 12 reflections in the range $35 < 2\theta < 39°$, for which the $\alpha_1\alpha_2$ doublet of Mo $K\alpha$ radiation was resolved.

Intensities of reflections were measured by the θ–2θ scan method with a scan speed of 1°(2θ) min^{-1} and a 10 s background count at the start and end of each scan. The intensities of three standard reflections (232,

226, 218) measured every 50 reflections were used to monitor X-ray damage and alignment of the crystal. Of 2062 unique reflections in the range $2\theta < 50°$, 209 were systematically absent, and 548 with $I < \sigma(I)$ were considered unobserved. The intensities were corrected for Lorentz and polarization factors, and for decay based on two different slopes: up to $\sin \theta/\lambda = 0.54$ Å^{-1} a maximum linear correction of 9% was applied and to the rest of the data ($0.54 < \sin \theta/\lambda < 0.60$ Å^{-1}) a maximum of 20%. Standard deviations for the structure factors were obtained from counting statistics (Wei & Ward, 1976). No corrections for absorption or extinction were made. Attenuation filters were used to keep the intensities within the linearity range of the counter.

Approximate scale and isotropic temperature factors were determined by Wilson's (1942) method. The structure was solved from the model of Robertson & Woodward (1938). The coordinates of seven C atoms at $y \sim 0$ were used to synthesize a Fourier map. This revealed the positions of 13 of the 14 C atoms. Successive difference syntheses improved the coordinates of all the C atoms and gave $R = \Sigma||F_o| - |F_c||/\Sigma |F_o| = 0.308$. At this point a full-matrix least-squares refinement with the program ORFLS (Busing, Martin & Levy, 1962) and unit weights lowered R to 0.141. A difference map revealed the positions of all H atoms. They were assigned isotropic temperature factors 1.25 Å^2 greater than those of the C atoms to which they were bonded. The resultant structure factor calculation had an R of 0.128. A least-squares cycle on the C atom coordinates and the scale factor lowered R to 0.112.

Anisotropic thermal parameters were introduced, and two cycles of refinement, one on anisotropic thermal parameters and one on the positional parameters of the C atoms, reduced R to 0.085. The coordinates of the H atoms were improved by another difference synthesis and R dropped to 0.072. The refinement was continued by weighted $[w = 1/\sigma(F)]$ least squares until the parameter shifts were insignificant compared with the estimated standard deviations.

The final R was 0.061 and $R_w = \{\Sigma[w(|F_o| - |F_c|)]^2/\Sigma(w|F_o|)^2\}^{1/2} = 0.036.$* In a final difference map, maximum and minimum residual densities were 0.13 and -0.23 e Å^{-3} respectively; these are insignificant when compared with an average peak height of 5.7 e Å^{-3} for the C atoms.

The scattering factors of Doyle & Turner (1968) were used for the C atoms, and of Stewart, Davidson & Simpson (1965) for the H atoms.

Discussion. The final atomic parameters are listed in Table 1, the atom notation is shown in Fig. 1, and bond distances and angles are listed in Table 2. Best least-squares planes were calculated for all the C atoms for molecules A and B; deviations from these planes are listed in Table 3. Best least-squares planes were also computed for the C atoms of each phenyl ring separately; these proved to be planar within the error of their determination (Table 3).

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* Lists of structure factors, anisotropic thermal parameters and H atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32840 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
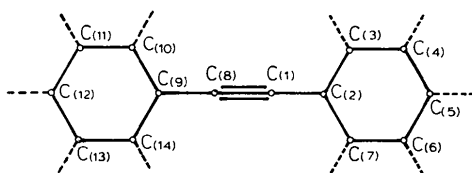

Fig. 1. The numbering system of tolane.

Table 1. *Final atomic parameters*

	x	y	z	Peak height (e Å^{-3})
Molecule A ($\frac{1}{2}$,0,0)				
C(1)	0·5496 (1)	0·0160 (4)	0·0244 (1)	6·2
C(2)	0·6697 (1)	0·0344 (4)	0·0804 (1)	6·4
C(3)	0·7118 (1)	0·2284 (4)	0·1350 (1)	5·4
C(4)	0·8274 (2)	0·2515 (4)	0·1851 (1)	5·3
C(5)	0·9010 (1)	0·0830 (4)	0·1821 (1)	5·3
C(6)	0·8601 (2)	−0·1103 (4)	0·1284 (1)	5·6
C(7)	0·7446 (2)	−0·1360 (4)	0·0778 (1)	5·7
Molecule B (0,0,$\frac{1}{2}$)				
C(1)	0·0260 (1)	−0·0304 (4)	0·4772 (1)	6·2
C(2)	0·0895 (1)	−0·0970 (3)	0·4227 (1)	6·2
C(3)	0·0691 (1)	−0·3053 (3)	0·3744 (1)	5·6
C(4)	0·1316 (2)	−0·3645 (4)	0·3230 (1)	5·4
C(5)	0·2141 (2)	−0·2198 (4)	0·3196 (1)	5·0
C(6)	0·2364 (1)	−0·0138 (4)	0·3681 (1)	5·3
C(7)	0·1744 (1)	0·0481 (4)	0·4194 (1)	6·4

The results confirm the general correctness of the structure reported by Robertson & Woodward (1938). The structure consists of two non-equivalent tolane molecules (A and B), each with a crystallographically imposed center of symmetry. The packing of the molecule is shown in Fig. 2 and is similar to that of *trans*-stilbene (Robertson & Woodward, 1937; Hoekstra, Meertens & Vos, 1975). The structures of the independent molecules are the same with approximate D_{2h} point symmetry. Mean molecular dimensions averaged over equivalent bonds are shown in Fig. 3

Table 2. *Bond distances (Å) and angles (°)*

	Molecule A	Molecule B
C(8)–C(1)	1·198 (3)	1·198 (4)
C(1)–C(2)	1·438 (3)	1·437 (4)
C(2)–C(3)	1·376 (3)	1·384 (3)
C(3)–C(4)	1·376 (4)	1·376 (4)
C(4)–C(5)	1·366 (4)	1·362 (4)
C(5)–C(6)	1·365 (3)	1·373 (3)
C(6)–C(7)	1·377 (3)	1·373 (4)
C(7)–C(2)	1·384 (3)	1·387 (4)
C(3)–HC(3)	0·98 (2)	0·95 (2)
C(4)–HC(4)	0·88 (2)	0·92 (2)
C(5)–HC(5)	0·96 (2)	0·94 (2)
C(6)–HC(6)	0·93 (2)	0·95 (2)
C(7)–HC(7)	0·91 (2)	0·99 (2)
C(8)–C(1)–C(2)	178·1 (2)	178·4 (2)
C(1)–C(2)–C(3)	120·8 (2)	121·4 (2)
C(2)–C(3)–C(4)	119·8 (2)	120·1 (2)
C(3)–C(4)–C(5)	120·7 (2)	120·4 (2)
C(4)–C(5)–C(6)	120·0 (2)	120·21 (2)
C(5)–C(6)–C(7)	120·0 (2)	120·0 (2)
C(6)–C(7)–C(2)	120·3 (2)	120·3 (2)
C(7)–C(2)–C(3)	119·2 (2)	119·0 (2)
C(7)–C(2)–C(1)	120·0 (2)	119·6 (2)
C(2)–C(3)–HC(3)	120·7 (12)	119·4 (12)
HC(3)–C(3)–C(4)	119·6 (12)	120·4 (12)
C(3)–C(4)–HC(4)	117·4 (14)	116·5 (13)
HC(4)–C(4)–C(5)	121·8 (14)	123·1 (13)
C(4)–C(5)–HC(5)	117·8 (13)	122·1 (15)
HC(5)–C(5)–C(6)	122·1 (13)	117·6 (15)
C(5)–C(6)–HC(6)	119·0 (13)	120·0 (13)
HC(6)–C(6)–C(7)	121·0 (13)	120·0 (13)
C(6)–C(7)–HC(7)	120·6 (13)	120·6 (11)
HC(7)–C(7)–C(2)	119·0 (13)	119·1 (11)

Table 3. *Deviations (Å) of tolane molecules and phenyl rings from least-squares planes*

	Molecule A	Molecule B	Phenyl ring A	Phenyl ring B
C(1)	−0·022	−0·002	–	–
C(2)	−0·037	0·005	0·003	0·005
C(3)	−0·025	−0·004	−0·002	−0·004
C(4)	0·012	−0·001	0·001	−0·000
C(5)	0·026	0·004	−0·001	0·004
C(6)	0·012	−0·004	0·002	−0·004
C(7)	−0·026	−0·001	−0·003	−0·001
σ	±0·027	±0·004	±0·003	±0·004

(the average bond scatter is 0·003 Å). The shortest intermolecular distance [between C(4) of molecule A and C(6) of molecule B] is 3·784 (4) Å; the distance between the corresponding H atoms is 2·70 (3) Å. Although the phenyl rings for both molecules are equally planar, molecule B shows a higher degree of planarity than molecule A (Table 3). This is because C(1) of the latter is 0·05 Å out of the least-squares plane defined by its phenyl ring. The planes defined by the two independent molecules make an angle of 49·2°.

The planar conformation of tolane in the crystal is not necessarily retained in solution or in the gas phase. In order to investigate this problem, semi-empirical, CNDO/2 quantum-mechanical calculations were carried out (Pople & Segal, 1966; Pople & Beveridge, 1970). Notwithstanding the fact that CNDO/2 calculations are only approximate, the method gives a reasonable description of the stereogeometry and overall electron distribution (Pople & Gordon, 1967). Standard bond lengths (Pople & Gordon, 1967) were

chosen to define the geometry: phenyl rings were assumed to be regular hexagons with C—C = 1·40, C—H = 1·08 and C(1)—C(2) = 1·45 Å. With a planar molecule the energy was minimized with respect to the length of the triple bond. For C≡C (1·19, 1·20, 1·21, 1·22 Å), the energies obtained are −105·8140, −106·8158, −106·8168 and −106·8170 a.u. respectively. From these values the minimum energy corresponds to 1·216 Å. With this last value, an energy calculation with one phenyl ring rotated by 90° with respect to the other was carried out. An energy rotation barrier of 0·65 kcal mol^{-1} was found, the perpendicular conformation being the more stable ($E = -106\cdot8180$ a.u.). The energy barrier thus obtained corresponds to a quasi free rotation of the phenyl ring around the C—C single bonds, and certainly no conclusion can be drawn for the conformation of tolane either in the gas phase or in solution. Spectroscopic Raman work in solution (Kellerer, Hacker & Brandmueller, 1971) favors the planar geometry.

Fig. 3 shows that all C—C distances in the phenyl ring are shorter that the value of 1·392 (10) Å obtained for benzene (Cox, Cruickshank & Smith, 1958). Part of this shortening, which increases systematically with distance from C(1), can be explained by thermal motion; this has been observed in similar molecular systems (Irngartinger, 1970, 1973; Jungk & Schmidt, 1971). Irngartinger (1970) attributes this effect entirely to differences in hybridization of the ring C atoms which carry H atoms.

The value of 1·438 (4) Å obtained for C(1)—C(2) agrees with values reported for C—C single bonds adjacent to a triple bond and a phenyl ring (Jungk & Schmidt, 1971; Jungk, 1972; Irngartinger, 1973). Nearly the same value, 1·428 Å, is obtained by considering a shortening of 0·112 Å of the single bond (1·540 Å) adjacent to a triple bond and a double bond (Bernstein, 1961). Robertson & Woodward (1938) report a value of 1·40 Å. From the equation $n = (2r_1 - 1\cdot84r_2 - 0\cdot16r_n)/(r_1 - 1\cdot84r_2 + 0\cdot84r_n)$ given by Pauling (1960), where $r_1 = 1\cdot504$, $r_2 = 1\cdot274$ and $r_n = 1\cdot438$ Å (present work), a bond number $n = 1\cdot18$ (i.e. 18% double-bond character) is obtained.

The 1·198 (2) Å obtained for the C—C triple bond distance agrees with the 1·203 Å reported for acetylene from spectroscopic results (Lafferty & Thibault, 1964). Jungk & Schmidt (1971) and Irngartinger (1973) report a value of 1·191 (2) Å for similar systems. The CNDO/2 method gives an optimum triple-bond distance of 1·216 Å for tolane. A similar calculation for acetylene (minimization of the energy with respect to the triple bond, while C—H is kept fixed at 1·08 Å) gives a triple-bond distance of 1·197 Å and a charge on the C atoms of −0·063 e. The corresponding value for tolane is −0·052 e (Fig. 3). A plausible conclusion is that the presence of the two phenyl rings does not appreciably disturb the character of the triple bond in this system.
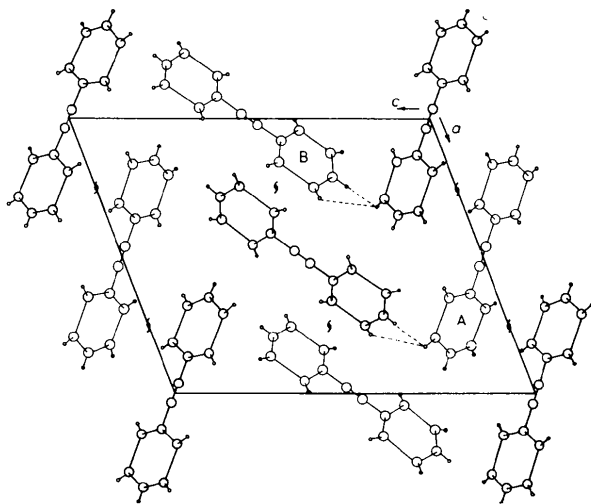

Fig. 2. The packing of tolane molecules viewed down **b**. Molecules having their centers at $y = 0$ and $y = \frac{1}{2}$ are shown with thin and thick lines respectively. The shortest intermolecular distances are shown with broken lines.
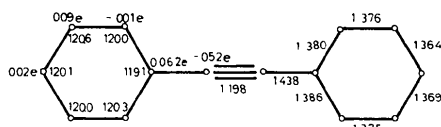

Fig. 3. Average bond distances (Å) and angles (°) of tolane and charge densities computed by the CNDO/2 method.

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High-Pressure Synthesis and Bond Lengths of Calcium Copper Germanium Oxide [CaCu₃](Ge₄)O₁₂

$$[CaCu_3](Ge_4)O_{12}$$

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Abstract. Single crystals of $[CaCu_3](Ge_4)O_{12}$ have been synthesized under high-pressure (50–70 kbar) and high-temperature (1000 °C) conditions. It has the cubic perovskite-like $[NaMn_3](Mn_4)O_{12}$ structure, $a = 7 \cdot 202$ Å, space group $= Im3$, $Z = 2$. The structure has been refined from single-crystal X-ray data. The average cation–oxygen distances are: Ca–O $= 2 \cdot 549$ (icosahedral coordination); Cu–O $= 1 \cdot 960$, $2 \cdot 677$, $3 \cdot 134$ (three sets of four O neighbours); Ge–O $= 1 \cdot 895$ Å (octahedral coordination).

Introduction. The three-cation mixed oxide $CaCu_3Ge_4O_{12}$ has been synthesized as part of a continuing program in this laboratory to investigate the series of compounds with the general formula $[AC_3](B_4)O_{12}$. These compounds have a perovskite-like arrangement and are usually cubic with a doubled

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lattice parameter with respect to the simple ABO_3 cubic perovskite. The brackets and the parentheses are used in order to show the relation between the two structures. The doubling of the unit cell is due to the order between the A and C cations and to a distortion of the O lattice consisting of a tilting of the O octahedra forming the three-dimensional corner-sharing network. This tilting distorts the 12-coordinated sites of the simple perovskite in such a way that the A cations are still surrounded by 12 equidistant O atoms arranged, however, as a slightly distorted icosahedron. On the other hand, the coordination polyhedra of the C cations consist of four close O atoms arranged as a square and four further away arranged as a rectangle perpendicular to the square. The other four O atoms around the C cations are arranged as a square perpendicular to the first two sets; however, these atoms are so far apart that they must be considered second nearest neighbours. The first two sets of O atoms form a polyhedron which can accommodate