1,3,5-Triphenylbenzene

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Abstract. $C_{24}H_{18}$; orthorhombic, $Pna2_1$; $Z=4$; $a=7.610$ (2), $b=19.765$ (2), $c=11.258$ (2) Å; $D_o=1.22$, $D_c=1.20$ g cm^{-3}. The parameters of the refined structure differ from those reported previously by Farag [*Acta Cryst.* (1954). **7**, 117–121]. The refined phenyl twist angles are 40·7, −37·2, and 36·1°.

Introduction. In crystalline diphenyl the phenyl rings are coplanar (Hargreaves & Rizvi, 1962). However, in crystalline p,p'-bitolyl the phenyl rings are twisted by 36 and 40° for the two molecules in the asymmetric unit. Williams (1972) has derived a conjugation potential function for p,p'-bitolyl by molecular packing analysis. It appeared that 1,3,5-triphenylbenzene was also an interesting compound in which to study the conjugation potential by molecular packing analysis. Farag (1954) reported the twist angles of the phenyl rings in this compound as $+34$, -27, and $+24°$. The errors in the structure determination were large, however, and it was necessary to take new X-ray diffraction data on 1,3,5-triphenylbenzene and further refine the structure.

The technical grade of 1,3,5-triphenylbenzene was obtained from Aldrich Chemical Company. The material was repeatedly crystallized from absolute ethanol to produce clear crystals with good face development. A single crystal of approximate dimensions $0.3 \times 0.3 \times 0.4$ mm was selected and mounted in a thin-walled glass capillary tube.

With vanadium-filtered Cr $K\alpha$ radiation ($\lambda = 2.2916$ Å), 10 reflection angles with high 2θ values were accurately measured and the lattice constants determined by least-squares extrapolation. The resulting values are $a=7.610$ (2), $b=19.765$ (2), and $c=11.258$ (2) Å. The calculated density for $Z=4$ was $D_c=1.20$ g cm^{-3}; the observed density was 1.22 g cm^{-3}. The observed extinctions were consistent with space group $Pna2_1$ as reported previously by Farag.

The intensities of 1691 independent reflections were measured by the $\theta-2\theta$ scan technique, with Cu $K\alpha$ radiation, on an Enraf–Nonius CAD-4 computer-controlled diffractometer at the University of Pittsburgh. Each measurement was the mean of reflection hkl and $\bar{h}kl$; the deviations between these equivalent reflections were observed to be very small. The data reduction was performed with the computer program of Shiono (1973).

The atomic positions of Farag were used as starting coordinates for the least-squares refinement (Busing, Martin & Levy, 1962). The scattering factors of Han-

son, Herman, Lea & Skillman (1964) were used for carbon, and of Stewart, Davidson & Simpson (1965) for hydrogen. The hydrogens were placed in calculated positions 1.097 Å from carbon, and along a line bisecting the C–C–C angle. Anisotropic temperature factors were used for carbon; the hydrogen temperature factors were set equal to the carbon to which they were attached. The z coordinate of C(6) was held constant to establish the origin in the polar direction; 216 parameters were refined in the non-centrosymmetric space group. The reflections were weighted as the inverse square of the estimated error of the observed structure factor amplitude. The refined weighted R index was 0.045.

Among the 24 most intense reflections, 18 had larger calculated structure factors than observed. An extinction correction was made (Zachariasen, 1963) and the structure was further refined to a final weighted R index of 0.042. The largest extinction correction was 26% for the 200 reflection.* The final difference Fourier map showed no peaks higher than 0.184 e Å^{-3}.

Discussion. The refined values of the structural parameters are shown in Table 1. Substantial shifts were obtained from the Farag parameters; the largest shift was 0.31 Å for C(23). The root-mean-square shift from the Farag positions was 0.145 Å. Fig. 1 shows the numbering of the atoms and the orientation of the thermal ellipsoids.

The observed bond distances in the four benzene rings range from 1.367 to 1.402 with a root-mean-square value of 1.387 and an observed standard deviation of 0.009 Å. This standard deviation was based on the assumption that all the ring distances are equal; it agrees well with the standard deviation of a C–C distance 0.011 Å calculated in the usual way from the inverse matrix of the normal equations. The ring–ring C–C distances are C(1)–C(7), 1.483; C(3)–C(13), 1.492; and C(5)–C(19), 1.485 Å. They are equal within experimental error; the mean value is 1.487 Å.

The deviations from planarity are of especial interest in this structure. Taken individually, each ring is a planar hexagon within experimental error. The equations of the best least-squares planes are as follows:

Plane C(1)–C(6):

$$0 \cdot 9812X + 0 \cdot 0943Y + 0 \cdot 1682Z = 2 \cdot 0671$$

Plane C(7)–C(12):

$$0 \cdot 8161X - 0 \cdot 5575Y + 0.3981Z = -0 \cdot 3981$$

Plane C(13)–C(18):

$$0 \cdot 9079X - 0 \cdot 2137Y + 0 \cdot 3607Z = 1 \cdot 2672$$

Plane C(19)–C(24):

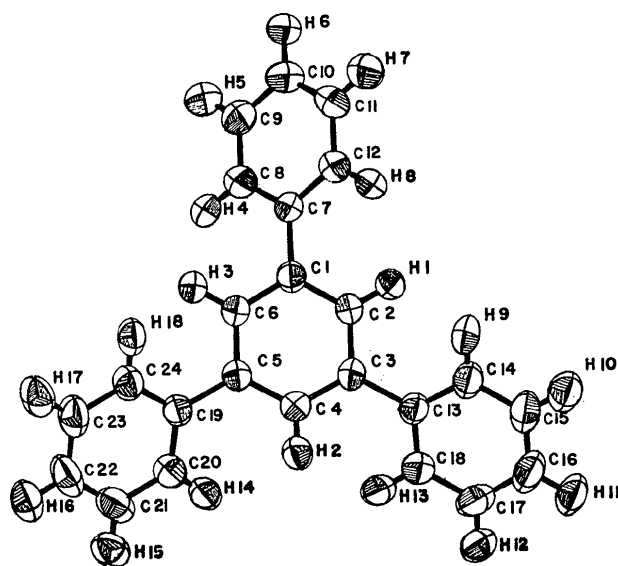$$0 \cdot 8551X + 0 \cdot 3971Y - 0 \cdot 3333Z = 3 \cdot 0960 \ .$$

Fig. 1. Molecular structure and thermal motion in crystalline 1,3,5-triphenylbenzene.

The out-of-plane bends may be measured by the deviations of C(7), C(10), C(13), C(16), C(19), and C(22) from plane C(1)–C(6). Ring C(13)–C(18) is not bent out-of-plane, within our experimental error. However, the other two rings are slightly bent out-of-plane with the following axial deviations: C(7), −0·028; C(10), −0·092; C(19), 0·027; and C(22), 0·120 Å. In addition to having the largest out-of-plane bend, ring C(19)–C(24) also has the largest in-plane bend of 1·1° as measured by the angle between the C(2)–C(5) and C(19)–C(22) vectors projected onto the C(1)–C(6) least-squares plane. The other two in-plane bends are both 0·2°, certainly a very small distortion from collinearity.

Because of the slight out-of-plane bend, the phenyl twist angles may simply be calculated as the angles between the least-squares planes; these angles are 40·7, −37·2, and 36·1°, respectively. If the two *gem*-carbon atoms are used to define the twist at each end, the angles are calculated as 40·9, −37·2, and 36·1°, which are not significantly different from the above.

The ring twists are sufficient to yield the following (calculated) intramolecular nonbonded H··· H distances (Fig. 1): H(1)–H(8), 2·35; H(1)–H(9), 2·28; H(2)–H(13), 2·24; H(2)–H(14), 2·28; H(3)–H(4), 2·30; and H(3)–H(18), 2·24 Å. The closest approaches between different molecules are at normal van der Waals distances.

Table 1. *Refined values* ($\times 10^4$) *of the parameters and their standard deviations in fractions of the unit cell*

The form of the temperature factor is $\exp(-\beta_{11} - \beta_{22} - \beta_{33} - 2\beta_{12} - 2\beta_{13} - 2\beta_{23})$. Hydrogens are listed on the same row as the attached carbon atom.

Atom	Carbon x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Hydrogen x	y	z
1	2192 (3)	1699 (1)	613 (3)	162 (5)	20 (1)	71 (2)	−1 (1)	−11 (3)	0 (1)			
2	2201 (4)	2306 (1)	−19 (3)	195 (6)	18 (1)	71 (2)	1 (2)	−1 (3)	−2 (1)	1977	2755	425
3	2509 (3)	2313 (1)	−1243 (3)	179 (5)	18 (1)	78 (2)	−3 (2)	2 (3)	3 (1)			
4	2811 (3)	1705 (1)	−1824 (3)	195 (6)	22 (1)	69 (2)	−2 (1)	4 (3)	0 (1)	3045	1712	−2729
5	2807 (3)	1089 (1)	−1218 (3)	177 (5)	20 (1)	72 (2)	1 (1)	7 (3)	0 (1)			
6	2500 (4)	1096 (1)	0	187 (5)	19 (1)	69 (2)	1 (2)	−5 (3)	2 (1)	2501	643	459
7	1828 (3)	1690 (1)	1909 (3)	182 (5)	19 (1)	65 (2)	4 (2)	−1 (3)	3 (1)			
8	809 (4)	1186 (1)	2411 (3)	226 (6)	26 (1)	77 (2)	−7 (2)	1 (3)	−2 (1)	307	806	1875
9	449 (4)	1179 (1)	3616 (4)	270 (7)	28 (1)	90 (3)	−9 (2)	33 (4)	5 (1)	−335	801	3975
10	1128 (4)	1675 (1)	4345 (3)	305 (8)	36 (1)	67 (2)	5 (2)	14 (4)	1 (1)	863	1673	5245
11	2162 (5)	2174 (2)	3867 (3)	293 (8)	31 (1)	78 (3)	−6 (2)	5 (4)	12 (1)	2682	2539	4423
12	2511 (4)	2190 (1)	2657 (3)	232 (7)	24 (1)	75 (2)	−8 (2)	1 (3)	−2 (1)	3283	2576	2312
13	2524 (3)	2963 (1)	−1915 (3)	186 (5)	21 (1)	76 (2)	7 (2)	19 (4)	3 (1)			
14	3184 (4)	3552 (1)	−1404 (3)	230 (6)	22 (1)	102 (3)	1 (2)	−7 (4)	6 (1)	3680	3544	−548
15	3184 (4)	4152 (1)	−2034 (4)	281 (8)	21 (1)	136 (4)	−1 (2)	13 (5)	7 (2)	3681	4589	−1655
16	2531 (5)	4177 (2)	−3165 (4)	358 (9)	26 (1)	120 (4)	19 (2)	44 (5)	20 (2)	2538	4630	−3623
17	1870 (5)	3599 (2)	−3687 (4)	376 (9)	36 (1)	77 (3)	24 (2)	20 (4)	14 (2)	1370	3618	−4543
18	1870 (4)	2994 (1)	−3063 (3)	299 (8)	27 (1)	79 (3)	10 (2)	22 (4)	1 (1)	1375	2562	−3459
19	3168 (3)	444 (1)	−1852 (3)	184 (5)	21 (1)	76 (2)	−3 (1)	18 (3)	−2 (1)			
20	2594 (4)	348 (1)	−3023 (3)	241 (6)	27 (1)	82 (3)	−8 (2)	11 (4)	−4 (1)	1881	722	−3453
21	2971 (4)	−246 (2)	−3625 (4)	284 (8)	35 (1)	93 (3)	−23 (2)	44 (4)	−17 (2)	2552	−311	−4492
22	3904 (4)	−755 (1)	−3078 (4)	271 (7)	26 (1)	132 (3)	−10 (2)	69 (5)	−21 (2)	4180	−1197	−3533
23	4463 (4)	−670 (1)	−1924 (4)	256 (7)	23 (1)	134 (4)	12 (2)	42 (5)	−3 (2)	5165	−1055	−1516
24	4097 (4)	−78 (1)	−1311 (4)	218 (6)	23 (1)	94 (3)	7 (2)	19 (3)	−3 (1)	4520	−24	−443

References

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1963). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.

FARAG, M. S. (1954). *Acta Cryst.* **7**, 117–121.

HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040–1044.

HARGREAVES, A. & RIZVI, S. H. (1962). *Acta Cryst.* **15**, 365–373.

SHIONO, R. (1973). Private communication.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

WILLIAMS, D. E. (1972). *Acta Cryst.* A**28**, 629–635.

ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Spermine Copper(II) Perchlorate

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Abstract.

$H_2N(CH_2)_3NH(CH_2)_4NH(CH_2)_3NH_2Cu(ClO_4)_2$, monoclinic, $P2_1/n$, $a = 16\cdot003$ (3), $b = 14\cdot701$ (4), $c = 7\cdot849$ (1) Å, $\beta = 91\cdot66$ (1)°, $Z = 4$, $D_c = 1\cdot67$ g cm^{-3}. Full-matrix least-squares refinement gave a final R of $8\cdot2\%$. The coordination about the copper ions is square planar of four nitrogen atoms of the same spermine molecule.

Introduction. The high level of spermine and spermidine in some human cancer sera has been demonstrated (Tsou, Lo, Selzer, Weinstein & Bender, 1973) with a cupric–cuprous sulfite method. To explore the physiological meaning of this *in vitro* reaction copper(II)–spermine chelates were prepared by Tsou, Lo & Miller (1973). Further studies by them indicated that whereas spermine stimulated growth in tissue culture systems of two tumor cell lines, the copper(II) chelate inhibited growth, suggesting a plausible non-immunogenic mechanism for retardation of tumor growth through ligand exchange of copper(II)-containing proteins with spermine. The X-ray structure determination was undertaken to confirm the nature of the chelate.

Lilac crystals, obtained by evaporation from 25% isopropanol in methanol, were supplied by Dr K. C. Tsou and Dr K. W. Lo. Precession photography indicated that they are monoclinic with the space group $P2_1/n$ uniquely determined by the systematic absences $h0l$, $h + l = 2n + 1$ and $0k0$, $k = 2n + 1$.

Data were collected on a Picker Nuclear FACS-I automated diffractometer using monochromatic Cu $K\alpha$ radiation. The θ–2θ scan technique was used out to a maximum $\sin \theta/\lambda$ of $0\cdot52$ with a scan rate of $1°$ min^{-1}, a base width of $1\cdot5°$ and a background time of 20 s. The data set consisted of 2804 reflections of which 858 were unobserved. All reflections having intensities less than $2\cdot33\sigma(I)$ were considered to be unobserved.

The coordinates of the copper(II) ion as well as those of the two chlorine atoms of the perchlorate ions were determined through three-dimensional Patterson synthesis and atomic superposition methods. For the latter the superposition programs by Hubbard & Jacobson (1969) were used. The remaining atoms were located through successive Fourier maps. The structure was isotropically refined with the UCLA full-matrix least-squares program to an R value of $10\cdot9\%$ and anisotropically refined to a final R value of $8\cdot2\%$. Hydrogen atoms were not located. The function minimized was $\sum w[|F_o| - (1/k)|F_c|]^2$ where k is the scale factor for the observed structure factors. The data were given weights inversely proportional to the standard errors of the observed structure amplitudes, where $\sigma[F_o(\mathbf{h})] = \{|F_o(\mathbf{h})|^2 + \sigma[I(\mathbf{h})]\}^{1/2} - |F_o(\mathbf{h})|$. The final positional parameters and anisotropic temperature factors,
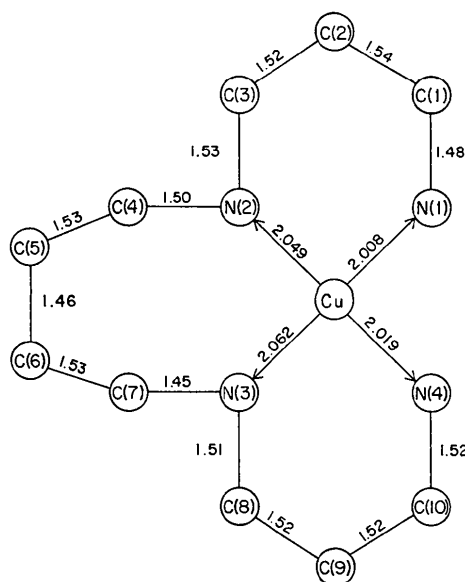

Fig. 1. Bond lengths in spermine copper(II) perchlorate.