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Refinement of the Crystal Structure of *trans*-Stilbene (TSB). The Molecular Structure in the Crystalline and Gaseous Phases

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The crystal structure of *trans*-stilbene (TSB) has been refined with intensities measured at −160°C on an AD3 Nonius diffractometer with Zr-filtered Mo radiation. The space group is $P2_1/a$ with $a = 12{\cdot}287$ (3), $b = 5{\cdot}660$ (3), $c = 15{\cdot}478$ (5) Å, $\beta = 112{\cdot}03$ (1)°. There are two independent molecules lying at inversion centres in the unit cell. The least-squares refinement has been based on 4761 independent reflexions, $R = 0{\cdot}07$. The crystals hardly show disorder in contrast to those recently studied [Finder, Newton & Allinger, *Acta Cryst.* (1974). B**30**, 411–415]. In the solid state the molecules are approximately planar, the average value of the C(ethylene)–C(phenyl) torsion angle φ is 5·2°. The value of $\langle\varphi^2\rangle^{1/2}$ for the TSB molecules in the gas phase (31 ± 5°) shows good agreement with the $\langle\varphi^2\rangle^{1/2}$ value predicted by *ab initio* calculations (28°). The bond lengths and angles are discussed.

Introduction

Two crystal structure determinations of *trans*-stilbene (TSB) have appeared in the literature. An early determination by Robertson & Woodward (1937) suffered from the fact that only comparatively inaccurate projection data were available, and a recent determination by Finder, Newton & Allinger (1974) showed disorder in the crystals.* We have refined the structure of TSB with data collected at −160°C as we are interested in the structure of molecules having a central C–C, C–N or N–N group with a varying number of phenyl groups linked to it. Other examples of this group of compounds are *N*-(diphenylmethylene)aniline (Tucker, Hoekstra, ten Cate & Vos, 1975), tetraphenylhydrazine, tetraphenylethylene and diphenylaminotriphenylmethane (Hoekstra, 1974).

Experimental

trans-Stilbene is commercially available (Fluka AG, Buchs SG; melting point 123–125°C). Crystals were obtained from a solution in ether by slow evaporation of the solvent. Only completely transparent crystals were considered. The present unit cell (*A*) is chosen differently from that of Robertson (*B*) and that of Finder (*C*). The relation between the axes is given by

$$\mathbf{a}(A)=\mathbf{a}(B),\ \mathbf{b}(A)=-\mathbf{b}(B),\ \mathbf{c}(A)=-\mathbf{a}(B)-\mathbf{c}(B)$$
$$\mathbf{a}(A)=\mathbf{c}(C),\ \mathbf{b}(A)=-\mathbf{b}(C),\ \mathbf{c}(A)=\mathbf{a}(C).$$

The cell dimensions were determined from zero-layer Weissenberg photographs calibrated with NaCl reflexion spots and taken at −160°C. The values obtained are $a = 12{\cdot}287$ (3), $b = 5{\cdot}660$ (2), $c = 15{\cdot}478$ (5) Å, $\beta = 112{\cdot}03$ (1)° [a(NaCl, 21°C) = 5·64006 Å, λ(Cu $K\alpha_1$) = 1·54050, λ(Cu $K\alpha_2$) = 1·54434 Å]. The space group is $P2_1/a$ with two sets of two molecules (α and β) lying at inversion centres.

For the intensity measurements a crystal with dimensions 0·5 × 0·5 × 0·3 mm and a mosaic spread smaller than 0·5° was used. The measurements were made on a Nonius diffractometer AD3 with Zr-filtered Mo radiation. The θ–2θ scan was applied with a scanning range of $(0{\cdot}72 + 0{\cdot}5\ \mathrm{tg}\,\theta)°$, and a counter aperture of 1·34°. The crystal was cooled in a stream of cold nitrogen gas (van Bolhuis, 1971). All independent reflexions with $0 < (\sin\theta)/\lambda < 0{\cdot}85$ Å^{-1} were collected at −160°C. Corrections for the variations in the intensity of the primary beam were made by use of the intensities of the reference reflexions $60\bar{1}$ and 026. Apart from a series of 400 reflexions where a variation in intensity of 7% was observed for the reference reflexions, the intensity fluctuations appeared to be smaller than 3%. Out of 5528 independent reflexions 4761 had a positive net intensity. Corrections were made for the intensity fluctuations of the incident beam and for the Lorentz and polarization effect, but not for absorption [μ(Mo $K\alpha$) = 0·73 cm^{-1}].

Attenuation filters were used to keep the intensities within the linearity range of the scintillation counter.

Refinement of the structure

The structure was easily obtained from a Patterson synthesis. For the refinement a block-diagonal least-squares program (Cruickshank, 1961) was used. The scattering factor for C was taken from Doyle & Turner (1968) and for H from Stewart, Davidson & Simpson

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* We have recently learnt that Dr J. Bernstein (University of the Negev, Israel) has also investigated the structure of TSB at room temperature. His results agree very closely with those of Finder *et al.* (1974), and a comparison of the two room temperature analyses will appear in *Acta Cryst.* Nevertheless we feel that the results of this low-temperature study are of interest. We thank Dr Bernstein for allowing us to see his paper before publication. The equilibrium conformation of TSB has recently been calculated by Warshel (1975).

(1965). For the C atoms anisotropic temperature factors were considered. The H atoms were put at geometrically reasonable positions. The C–H distances were kept fixed at 1·08 Å and isotropic temperature parameters were used. During the latter stages of the refinement the weighting scheme $w=[w_c^{-1}+p^2|F_o|^2]^{-1}$, with w_c the weight due to counting statistics, was used. $p^2=6\times10^{-4}$ was chosen so that the variation of $\langle w|\Delta F|^2\rangle$ as a function of $|F_o|$ was kept as small as possible (the remaining variation is approximately a factor of two). For the 4761 reflexions on which the refinement is based, $R_w=[\sum w(F_o-F_c)^2/\sum w|F_o|^2]^{1/2}$ is 0·086 (R=0·070). The final coordinates and thermal parameters are listed in Table 1.*

At the end of the refinement difference syntheses were calculated with the low-order [$(\sin\theta)<0·6$ Å^{-1}] and the high-order [$(\sin\theta)/\lambda\geq0·6$ Å^{-1}] reflexions. For the β-molecule no unusual features are observed. As can be seen from Fig. 1 the high-order map is flat, whereas the low-order map shows the usual bonding maxima. For the α molecule, on the other hand, the excess density in the low order map is not maximal on the centre of the C–C double bond and the high order map is not flat. We have tentatively ascribed the extra maxima in the difference map to disorder. The difference map of Fig. 1(*c*) shows that the disorder for the α molecule is similar to that proposed for *p*-azotoluene

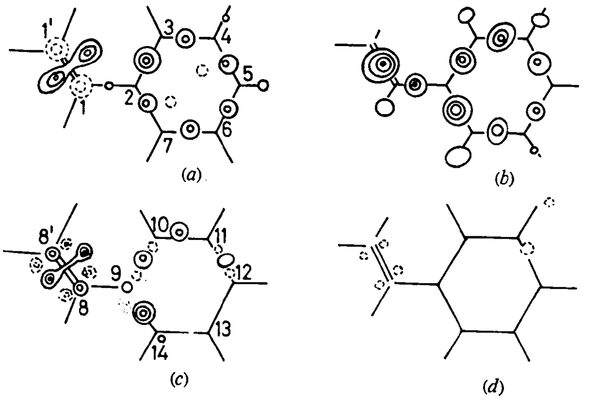

Fig. 1. Difference Fourier syntheses at the end of the refinement (see text). (*a*) low-order map α molecule, (*b*) low-order map β molecule, (*c*) high-order map α molecule, (*d*) high-order map β molecule. The difference densities are shown for the best plane through the phenyl ring and for the plane of the ethylene group. Contours are given at intervals of 0·1 e Å^{-3}, positive contours start at 0·2 e Å^{-3}, negative contours (dashed lines) at $-0·2$ e Å^{-3}, $\sigma=0·06$ e Å^{-3}.

Table 1. *Final parameters*

For the numbering of the atoms, see Fig. 4. The second index for a hydrogen atom corresponds with the heavy atom to which it is linked. Standard deviations are given, in parentheses, in units of the last decimal place. The anisotropic temperature factor is defined as

$$T(hkl)=\exp\,[-2\pi^2(U_{11}a^{*2}h^2+U_{22}b^{*2}k^2+U_{33}c^{*2}l^2+2U_{12}ha^*kb^*+2U_{23}kb^*lc^*+2U_{13}ha^*lc^*)].$$

	x	y	z
C(1)	0·03269 (9)	0·07731 (21)	0·03139 (8)
C(2)	0·16059 (9)	0·06342 (20)	0·08282 (7)
C(3)	0·21595 (10)	0·24984 (21)	0·14250 (8)
C(4)	0·33629 (10)	0·24871 (22)	0·19234 (8)
C(5)	0·40447 (10)	0·06084 (23)	0·18451 (8)
C(6)	0·35110 (10)	−0·12583 (21)	0·12513 (8)
C(7)	0·23041 (10)	−0·12515 (21)	0·07443 (8)
C(8)	0·00337 (8)	0·59931 (18)	0·47749 (7)
C(9)	0·07904 (8)	0·63683 (17)	0·42425 (6)
C(10)	0·16362 (8)	0·47218 (18)	0·42208 (7)
C(11)	0·23100 (9)	0·51507 (20)	0·36880 (8)
C(12)	0·21627 (9)	0·72233 (20)	0·31681 (8)
C(13)	0·13383 (10)	0·88857 (20)	0·31943 (8)
C(14)	0·06670 (9)	0·84624 (19)	0·37295 (7)

	x	y	z	B (Å^2)
H(15-1)	−0·01340	0·22522	0·04398	2·6 (4)
H(16-3)	0·16332	0·39623	0·14927	2·9 (4)
H(17-4)	0·37756	0·39363	0·23828	3·3 (4)
H(18-5)	0·49807	0·05935	0·22382	2·6 (3)
H(19-6)	0·40374	−0·27222	0·11838	2·7 (4)
H(20-7)	0·18915	−0·27025	0·02860	3·0 (4)
H(21-8)	−0·05171	0·74491	0·48070	2·3 (3)
H(22-10)	0·17509	0·31116	0·46176	2·4 (3)
H(23-11)	0·29496	0·38609	0·36714	1·8 (3)
H(24-12)	0·26870	0·75519	0·27555	2·1 (3)
H(25-13)	0·12234	1·04953	0·27951	2·6 (3)
H(26-14)	0·00275	0·97522	0·37462	2·3 (3)

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
C(1)	0·0185 (4)	0·0218 (5)	0·0212 (5)	−0·0027 (7)	−0·0044 (8)	0·0162 (7)
C(2)	0·0171 (4)	0·0220 (4)	0·0153 (4)	−0·0047 (7)	0·0002 (7)	0·0131 (6)
C(3)	0·0211 (4)	0·0222 (5)	0·0226 (5)	−0·0026 (8)	−0·0076 (8)	0·0185 (8)
C(4)	0·0229 (5)	0·0254 (5)	0·0206 (5)	−0·0099 (8)	−0·0108 (8)	0·0143 (8)
C(5)	0·0179 (4)	0·0299 (5)	0·0178 (4)	−0·0026 (8)	0·0042 (8)	0·0112 (7)
C(6)	0·0225 (5)	0·0241 (5)	0·0225 (5)	0·0080 (8)	0·0044 (8)	0·0208 (8)
C(7)	0·0217 (5)	0·0218 (5)	0·0193 (4)	−0·0050 (8)	−0·0059 (7)	0·0159 (7)
C(8)	0·0141 (4)	0·0172 (4)	0·0166 (4)	0·0020 (6)	0·0049 (6)	0·0126 (6)
C(9)	0·0130 (3)	0·0151 (4)	0·0137 (4)	−0·0008 (6)	0·0017 (6)	0·0087 (6)
C(10)	0·0148 (4)	0·0163 (4)	0·0184 (4)	−0·0002 (6)	0·0002 (7)	0·0130 (6)
C(11)	0·0163 (4)	0·0202 (4)	0·0209 (4)	−0·0007 (7)	−0·0020 (7)	0·0184 (7)
C(12)	0·0200 (4)	0·0223 (5)	0·0191 (4)	−0·0080 (7)	−0·0009 (7)	0·0201 (7)
C(13)	0·0231 (5)	0·0187 (4)	0·0190 (4)	−0·0054 (7)	0·0034 (7)	0·0183 (7)
C(14)	0·0188 (4)	0·0156 (4)	0·0182 (4)	0·0019 (7)	0·0049 (7)	0·0149 (7)

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* A table of calculated and observed structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31106 (16 pp., 1 microfiche). Copies may be obtained from The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

by Brown (1966; Fig. 2). In contrast to the strong disorder in the *p*-azotoluene crystals studied by Brown and in the TSB crystals studied by Finder *et al.* (1974), in our TSB crystals the second orientation of the α molecule is present to only a few per cent.

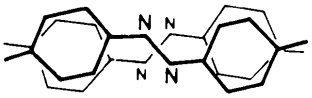


Fig. 2. Superposition of two centrosymmetric *p*-azotoluene molecules (Brown, 1966). The N–N bonds are approximately perpendicular to each other.

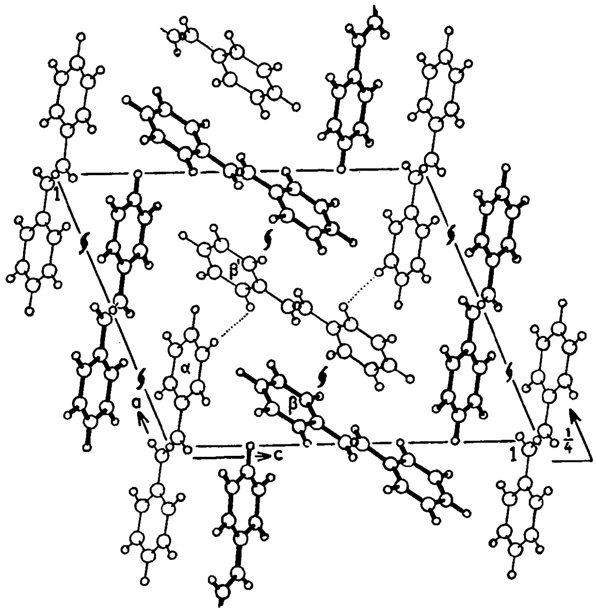


Fig. 3. Projection along the monoclinic *b* axis. Molecules having their centres at $y=0$ and $y=\frac{1}{2}$ are drawn with thin and thick lines respectively. The intermolecular distance given is H(α, $y=0$)···H(β', $y=1$)=2·222 Å.

The molecular structure in the solid and in the gaseous state

The packing of the molecules is shown in Figs. 3 and 4. There is only one intermolecular distance shorter than the relevant sum of the van der Waals radii. This H···H distance of 2·222 Å is given in Fig. 3. In the **b** direction there are columns of α molecules around $[0,y,0]$ and $[\frac{1}{2},y,\frac{1}{2}]$ and columns of β molecules around $[\frac{1}{2},y,0]$ and $[0,y,\frac{1}{2}]$. Within a column successive molecules are obtained by translation in the **b** direction. From Fig. 5 it can be seen that the packing of the molecules is not the same for the two columns.

The bond lengths and angles in the two independent centrosymmetric molecules are listed in Fig. 6. The standard deviations in the bond lengths and angles as obtained from the variance–covariance matrix of the coordinates (Darlow, 1960) are 0·0015 Å for C–C and 0·11° for C–C–C. Owing to the disorder described above we have multiplied these values by a factor of two for the α molecule. Corresponding bond lengths and C–C–C valence angles in the two molecules do not show significant differences. The disorder of the α molecules is so small that it does not affect the thermal parameters to a large extent. The value of $\langle U_{ii}^2(\text{principal axis})\rangle^{1/2}$ for the C atoms is 0·0217 Å² for the α and 0·0177 Å² for the β molecules.

Comparison with the earlier structure determinations shows that the present work has a considerably higher accuracy. The two centrosymmetric molecules are approximately planar. The torsion angle φ around the C–C(phenyl) bond is 3·4° for the α and 6·9° for the β molecule. The C_6H_5–C groups show only small devia-

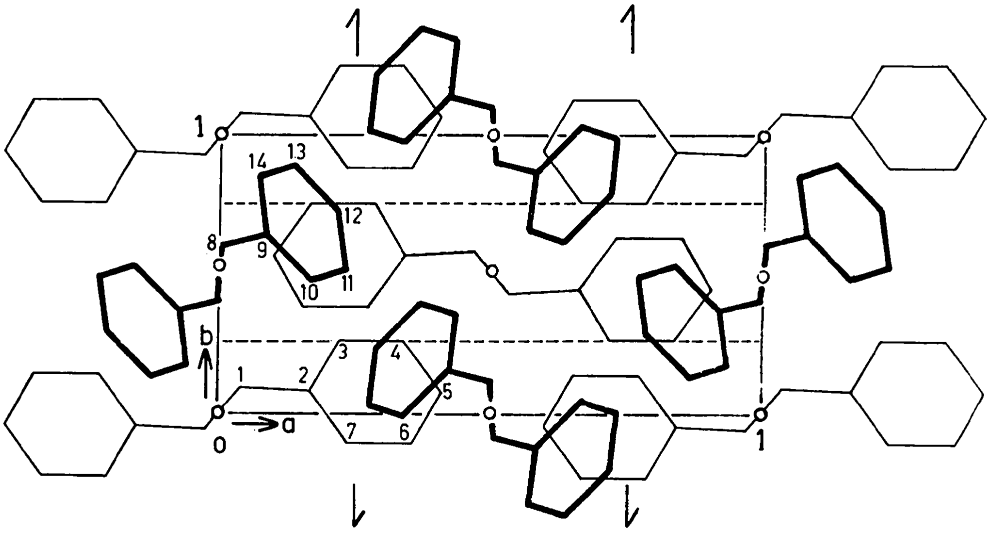


Fig. 4. Projection along [001] onto the plane (001). The α molecules having their centres at $z=0$ are drawn with thin lines, the β molecules having their centres at $z=\frac{1}{2}$ are given with thick lines.

tions from planarity. Only for C(8) is the distance (0·04 Å) to the C_6H_5 plane larger than 0·01 Å.

The weighted average value of the double bond, 1·338 Å, is slightly smaller and that of the adjacent C–C bond, 1·472 Å, slightly larger than the corresponding values, 1·356 and 1·458 Å, found in a PPP calculation (Pariser & Parr, 1953; Pople, 1953). The parameters required for the calculation and the bond length-bond order curve used were taken from Nishimoto & Forster (1966); for details see Hoekstra (1974).

The valence angles in the molecules are largely determined by intramolecular repulsions between nonbonded atoms (Bartell, 1968). As the α and β molecules are very similar, the discussion will be restricted to the β molecules; for H(21) the position derived from the gas electron diffraction study will be used (Fig. 6). The values of the bond lengths and angles around C(8) are such that the distances C(8′)···H(21) = 2·13 Å, C(9)···H(21) = 2·11 Å and C(8′)···C(9) = 2·50 Å are approximately equally shortened in comparison with the sum of the relevant van der Waals radii (1·7 Å for C and 1·0–1·2 Å for H; Pauling, 1960; Mack, 1932; Mack, 1937). To diminish the repulsion between C(10′) and C(8) the angle C(10′)–C(9′)–C(8′) is larger than the angle C(14′)–C(9′)–C(8′). In the approximately planar molecule (φ = 6·9°) the distance C(10′)···C(8)

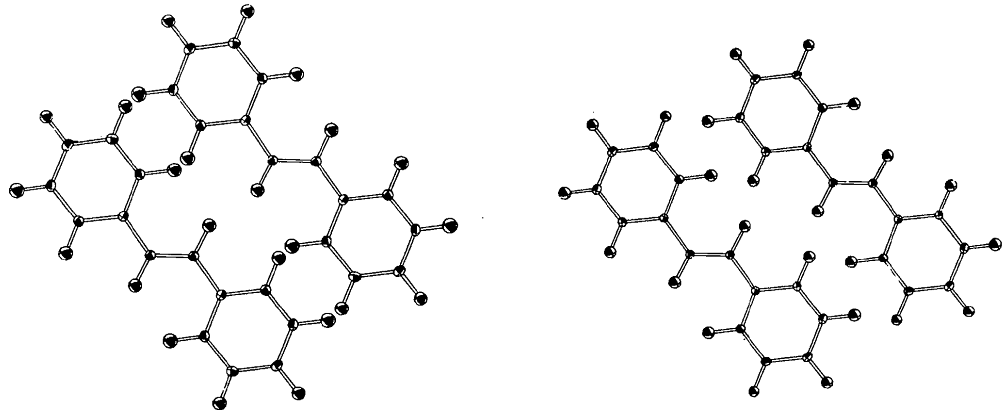
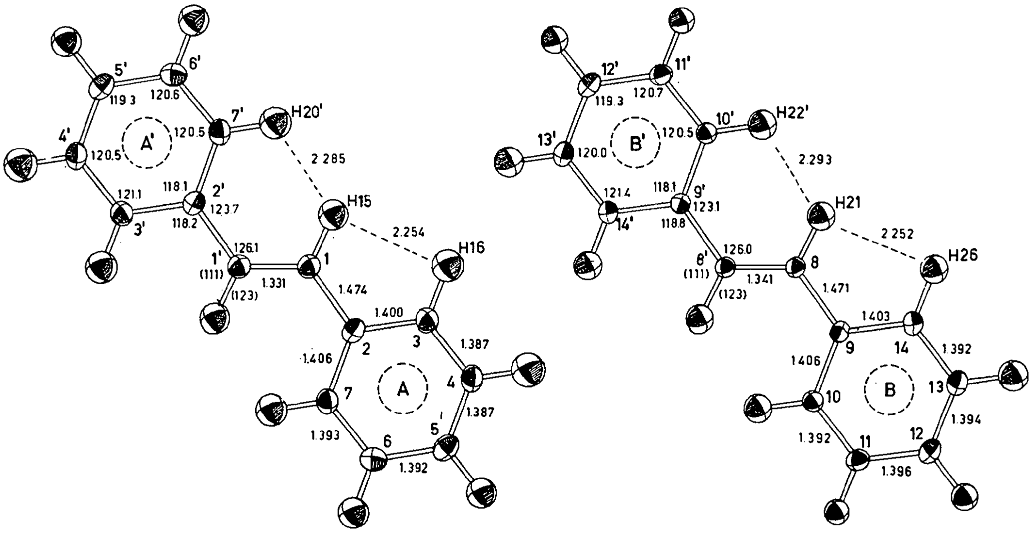

(*a*) (*b*)

Fig. 5. (*a*) Projection of two successive α molecules in the **b** direction along the normal to the ethylene plane onto the ethylene plane. (*b*) Analogous projection for the β molecules. In the projection shown successive α molecules are shifted by 4·96 Å along a vector making an angle of 40° with the C=C bond, for the β molecules these numbers are 5·33 Å and 28°.



α MOLECULE β MOLECULE

Fig. 6. Bond lengths, valence angles, and thermal ellipsoids (50% probability) for the two independent centrosymmetric TSB molecules. Corrections for libration have not been applied. The angles C=C–H and C–C–H in parentheses are derived from the gas electron diffraction study by Trætteberg, Frantsen, Mijlhoff & Hoekstra (1975).

is 0·37 Å shorter than the van der Waals distance of 3·4 Å. This distance can be enlarged by increasing φ. That this does not occur suggests that the molecule tends to be planar, presumably to maximize the delocalization energy.

Ab initio calculations have been done to obtain the energy as a function of φ (Hoekstra, 1974). We have performed the calculations for the model compound styrene in which one of the phenyl groups of TSB is replaced by an H atom. A minimum STO-3G basis set has been used [for details see Hoekstra (1974)]. The $E(\varphi)$ curve obtained is in good agreement with the theoretical curve recently published by Almlöf, Isacsson, Mjöberg & Ralowski (1974) for styrene with an angle C=C–C = 127°. The curve appears to have a very flat minimum around $\varphi = 0°$; for a temperature of 20 °C φ varies from -36 to $+36°$ in the energy range $E(\text{min})$ to $E(\text{min}) + kT$. For TSB itself a similar flat energy curve is expected as the two phenyl rings are at large distances from each other. The curve for TSB may, however, be somewhat steeper than for styrene due to an extra gain in delocalization energy for small values of φ. Because of the small variation in $E(\varphi)$ discussed above, the φ values of the TSB molecules in the crystal will be largely determined by intermolecular forces. Due to these forces the librations of the phenyl rings are small. In a rigid body analysis (Cruickshank, 1956) r.m.s. librations of 2·96 and 2·31° (at -160 °C) were found around directions approximately coinciding with C(5)–C(5′) for the α and with C(12)–C(12′) for the β molecule. These librations are due both to librations of the molecule as a whole and to independent librations of the individual phenyl rings.

The structure of TSB has also been studied in the gas phase at 280 °C and at 190 °C (Trætteberg, Frantsen, Mijlhoff & Hoekstra, 1975). In this study a value of 31 ± 5° has been reported for φ. This value should, however, be interpreted as a $\langle\varphi^2\rangle^{1/2}$ value as in an electron diffraction study only average atomic distances are observed, whereas in TSB distances which depend on φ, such as C(1)···C(7′), vary with φ^2 in good approximation (the small difference between the average distances r_g and the related r_a values as defined by Bartell (1972), can be neglected for the present qualitative discussion). For styrene we have calculated from the theoretical $E(\varphi)$ curve, assuming a Boltzmann distribution, which value of $\langle\varphi^2\rangle^{1/2}$ is to be expected for the gas phase at 280 °C. The result, 28°, agrees nicely with the results of the electron diffraction work on TSB. The bond lengths and valence angles observed for the TSB molecules in the gas phase are not sufficiently accurate to make a comparison with the molecules in the solid state worth while.

Finally is should be noticed that in principle the widths $\langle(r-r_g)^2\rangle$ (called u^2 in electron diffraction work) of the peaks in the radial distribution function should show whether or not φ has a fixed value. For the distance C(1)···C(7′) in TSB the width increases by 0·008 Å^2 if for φ a Gaussian distribution function with $\langle\varphi^2\rangle^{1/2} = 30°$ rather than a fixed value of 30° is assumed (Hoekstra, 1974). Especially for large molecules it is not possible to determine this small increase with certainty, as the radial distribution curve shows a strong overlap for the peaks at large values of r.

References

Almlöf, J. E., Isacsson, P. U., Mjöberg, P. J. & Ralowski, W. (1974). *Chem. Phys. Lett.* **26**, 215–217.

Bartell, L. S. (1968). *J. Chem. Educ.* **45**, 754–767.

Bartell, L. S. (1972). In *Physical Methods in Chemistry*, Vol. III. Ch. 2, pp. 125–159. New York: Wiley–Interscience.

Bolhuis, F. van (1971). *J. Appl. Cryst.* **4**, 263–264.

Brown, C. J. (1966). *Acta Cryst.* **21**, 153–158.

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 747–758.

Cruickshank, D. W. J. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*. London: Pergamon Press.

Darlow, S. F. (1960). *Acta Cryst.* **13**, 683–683.

Doyle, P. A. & Turner, P. S. (1968). *Acta Cryst.* A**24**, 390–397.

Finder, C. J., Newton, M. G. & Allinger, N. L. (1974). *Acta Cryst.* B**30**, 411–415.

Hoekstra, A. (1974). Thesis, Univ. of Groningen.

Mack, E. (1932). *J. Amer. Chem. Soc.* **54**, 2141–2165.

Mack, E. (1937). *J. Phys. Chem.* **41**, 221–231.

Nishimoto, K. & Forster, L. S. (1966). *Theoret. Chim. Acta*, **4**, 155–165.

Pariser, R. & Parr, R. G. (1953). *J. Chem. Phys.* **21**, 466–471, 767–776.

Pauling, L. (1960). In *The Nature of the Chemical Bond*, 3rd ed., p. 260. Ithaca: Cornell Univ. Press.

Pople, J. A. (1953). *Trans Faraday Soc.* **49**, 1375–1385.

Robertson, J. M. & Woodward, I. (1937). *Proc. Roy. Soc.* A**162**, 568–583.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Trætteberg, M., Frantsen, E. B., Mijlhoff, F. C. & Hoekstra, A. (1975). *J. Mol. Struct.* **26**, 57–68.

Tucker, P. A., Hoekstra, A., ten Cate, J. M. & Vos, A. (1975). *Acta Cryst.* B**31**, 733–757.

Warshel, A. (1975). *J. Chem. Phys.* **62**, 214–221.