

range of values reported for thioamides (Walter & Vos, 1970).

The long C(1)–C(2) bond of 1.53 Å, and the 92° torsion angle are consistent with the high coalescence temperature reported by Fulea & Krueger. Since there is no cross-conjugation between the benzoyl and thiono groups, barrier reduction of the type reported in dimethylthiobenzamide cannot occur. On the contrary, it seems likely that the inductive effect of the electro-positive carbonyl would enhance the barrier. These two effects would explain why the title compound apparently has one of the highest C–N rotational barriers so far encountered in thioamides.

The authors would like to thank Dr P. J. Krueger for providing the sample and Dr Penelope Codding for preparing the diagrams.

*Acta Cryst.* (1979). **B35**, 785–788

## ***o*-Terphenyl by Neutron Diffraction\***

BY GEORGE M. BROWN AND H. A. LEVY

*Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, USA*

(Received 31 August 1978; accepted 30 October 1978)

**Abstract.** C<sub>18</sub>H<sub>14</sub>, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 18.583 (3), *b* = 6.024 (1), *c* = 11.728 (2) Å (at 295–297 K, by neutron diffraction, based on *a* = 5.64037 Å for NaCl), *Z* = 4,  $\rho_c = 1.65 \text{ Mg m}^{-3}$  [*cf.* Clews & Lonsdale (1937). *Proc. R. Soc. London Ser. A*, **161**, 493–504]. One of the end rings is twisted 42.1 and the other 62.1° in the same sense from the (physically impossible) conformation with all three rings coplanar. Other consequences of overcrowding in the molecule are shown by the significant bending, in and out of the ring planes, at the ends of the inter-ring bonds C(1)–C(1') and C(1'')–C(2') (IUPAC atom numbering rules). Angles C(1)–C(1')–C(2') and C(1'')–C(2')–C(1') are opened to 123.6 (3) and 123.0 (3)°.

**Introduction.** A crystal specimen† was shaped to an approximate rectangular parallelepiped ~4.8 × 3.5 × 3.7 mm (61.4 mm<sup>3</sup>, 68.5 mg), carefully examined for quality by X-ray precession photography, enclosed in a

## References

- BROWN, B. T. & KATEKAR, G. F. (1969). *Tetrahedron Lett.* **28**, 2343–2344.  
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.  
 KRUEGER, P. J. & FULEA, A. O. (1975). *Tetrahedron*, **31**, 1813–1816.  
 NEUMAN, R. C. & YOUNG, L. B. (1965). *J. Phys. Chem.* **69**, 2570–2576.  
 SANDSTRÖM, J. (1967). *J. Phys. Chem.* **71**, 2318–2325.  
 SCHWENKER, G. & ROSSWAG, H. (1967). *Tetrahedron Lett.* **43**, 4237–4238.  
 WALTER, W. & VOS, J. (1970). *The Chemistry of Amides*, edited by J. ZABICKY, pp. 383–475. London: Interscience.

thin-walled quartz tube to prevent sublimation, and mounted on the neutron diffractometer at the Oak Ridge High Flux Isotope Reactor. The cell parameters (see *Abstract*) were determined by the least-squares method from the first moments of 108 neutron  $2\theta$  scans ( $70.1 < 2\theta < 83.4^\circ$ ). Standard procedures (Lisensky, Johnson & Levy, 1976; Spirlet & Busing, 1978) were used to collect intensity data for the 1891 independent reflections of one octant of reciprocal space to the  $(\sin \theta)/\lambda$  limit  $0.665 \text{ \AA}^{-1}$  ( $\lambda = 1.0155 \text{ \AA}$ ). Absorption corrections on  $|F_o|^2$  ranging from 1.795 to 1.996 were computed by Gaussian integration (Busing & Levy, 1957). The coefficient used,  $\mu = 0.1924 \text{ mm}^{-1}$ , was obtained by calculation using the total scattering cross-section  $551 \text{ fm}^2$  for C (*International Tables for X-ray Crystallography*, 1962) and the cross-section  $3800 \text{ fm}^2$  for H. The latter has been found empirically to yield good approximations to  $\mu$  for hydrogenous compounds. The solution for the structure was obtained with ease by use of the 210 *E* values  $>1.50$  and the direct-method program *MULTAN* of Main, Woolfson & Germain (1971), the indicated best set of phases yielding all 18 C atoms among the highest 22 peaks of the *E* map. Approximate coordinates for the 14 H

\* Research sponsored by the Division of Materials Sciences, US Department of Energy, under contract W-7405-eng-26 with the Union Carbide Corporation.

† Crystals were kindly supplied by Professor Joseph Lang of Thomas More College, Covington, Kentucky.

atoms were calculated from the C atom coordinates, and full-matrix least-squares refinement was started at once. In the final cycles, an isotropic extinction parameter (Coppens & Hamilton, 1970) was adjusted along with the scale factor, the coordinates, and the anisotropic thermal parameters (290 parameters in all). The 496 reflections having  $|F_c|^2$  less than  $\sigma(F_o|^2)$  were weighted zero; otherwise the weights used for the  $|F_o|^2$  observational data were the reciprocals of the variances, which were computed as  $\sigma^2(|F_o|^2) = [\sigma_c^2(|F_o|^2) + (0.03|F_o|^2)^2]$ , where  $\sigma_c^2(|F_o|^2)$  is the purely statistical variance. The nuclear scattering lengths used are from a compilation by Shull (1972):  $b_C = 0.6648$ ,  $b_H = -0.374 \times 10^{11}$  mm. The final values of the usual measures of goodness of fit for the reflections not weighted zero are:  $R(F) = 0.059$ ,  $R(F^2) = 0.057$ ,  $R_w(F^2) = 0.075$ ,  $\sigma_1 = 1.005$  (e.s.d. of observation of unit weight). The value of the isotropic extinction parameter  $g$ , as defined by Coppens & Hamilton (1970), is  $0.36(2) \times 10^4 \text{ rad}^{-1}$ . Table 1 lists the atom coordinates and their estimated standard errors.\*

In a final difference Fourier synthesis including only the reflections weighted non-zero in the refinement the densities ranged from  $-0.053$  to  $+0.052$  in units of  $10^{-11} \text{ mm } \text{Å}^{-3}$ , to be compared with peak densities in the corresponding final Fourier map of 1.40 to 2.53 for C atoms and  $-0.48$  to  $-0.84$  for H atoms.

**Discussion.** The molecular conformation† and the orientation of the molecule in the unit cell (see the

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34017 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† The molecule depicted in Figs. 1 and 2 has the chirality implied by the coordinates of Table 1. The analysis of course does not distinguish between this chirality and the opposite one of the inverted structure.

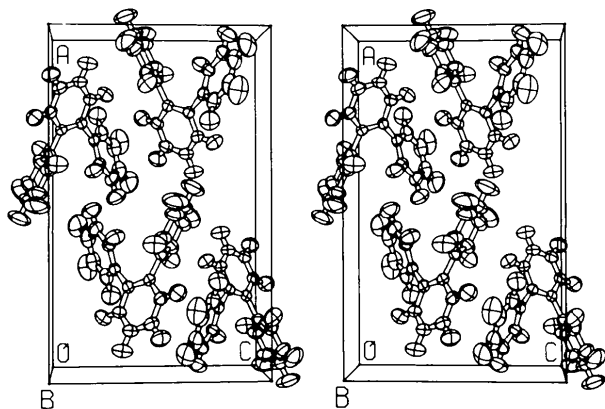


Fig. 1. Stereoscopic drawing showing the packing of molecules in the *o*-terphenyl crystal. Atoms are represented by their ellipsoids of 50% probability (Johnson, 1976). The shortest intermolecular distances (in no way unusual) are: C...C, 3.60; C...H, 2.82; H...H, 2.42 Å.

packing drawing of Fig. 1) are consistent with the predictions made by Clews & Lonsdale (1937) from a study of the diamagnetic anisotropy of the crystal, to the degree that the predictions were precise. The complete description of the structure from the present work will be useful in interpreting on a molecular basis the results of remeasurements of diamagnetic susceptibility now in progress (Lang, 1978).

Bond lengths, valence angles, and other details of the molecular structure are shown in Fig. 2. The angles  $\phi$  in the figure are twists about the inter-ring bonds from the theoretical conformation (not physically possible) in which all three rings are coplanar. These angles are pure twists, each having been calculated as the angle less than  $90^\circ$  between the projections on the plane perpendicular to an inter-ring bond of the normals to the least-squares best planes through the central ring of six C atoms and through the appropriate terminal ring. The negative signs make the angles conform to the sign convention for torsion angles (Klyne & Prelog, 1960). The deviation of each C and H atom from the least-squares best plane through its own ring of six C atoms is shown. For each of the four axial C and two axial H

Table 1. Fractional atomic coordinates for *o*-terphenyl ( $\times 10^5$ )

Estimated standard errors are given in parentheses.

	<i>x</i>	<i>y</i>	<i>z</i>
C(1)	31081 (15)	67820 (51)	29788 (21)
C(2)	38203 (17)	73379 (64)	27147 (25)
C(3)	42515 (21)	58664 (74)	21046 (31)
C(4)	39846 (29)	38499 (75)	17346 (35)
C(5)	32770 (30)	33043 (72)	19845 (36)
C(6)	28500 (23)	47356 (66)	26038 (29)
C(1')	26282 (15)	83903 (58)	35778 (22)
C(2')	28475 (14)	96847 (53)	45093 (22)
C(3')	23711 (17)	112479 (65)	49743 (29)
C(4')	16818 (18)	115164 (78)	45436 (31)
C(5')	14560 (17)	102040 (84)	36402 (32)
C(6')	19260 (15)	86778 (74)	31676 (27)
C(1'')	35622 (15)	94537 (56)	50560 (25)
C(2'')	40329 (19)	112382 (70)	50792 (36)
C(3'')	47019 (21)	110422 (92)	55979 (43)
C(4'')	49087 (23)	90850 (115)	61008 (40)
C(5'')	44339 (25)	72927 (103)	60989 (37)
C(6'')	37654 (20)	74857 (74)	55712 (29)
H(2)	40380 (38)	89221 (141)	29738 (75)
H(3)	48015 (45)	63294 (197)	19117 (82)
H(4)	43400 (64)	27165 (193)	12343 (87)
H(5)	30671 (76)	17199 (167)	16973 (93)
H(6)	22942 (48)	42362 (153)	28183 (80)
H(3')	25482 (41)	122439 (140)	56864 (62)
H(4')	13311 (44)	127293 (203)	49235 (83)
H(5')	9177 (37)	103966 (206)	32705 (88)
H(6')	17489 (37)	76886 (182)	24271 (68)
H(2'')	38799 (46)	127805 (157)	46638 (90)
H(3'')	50662 (48)	124572 (238)	55903 (105)
H(4'')	54327 (47)	89058 (240)	64977 (99)
H(5'')	45846 (64)	57317 (214)	65036 (98)
H(6'')	33933 (51)	60963 (152)	55534 (81)

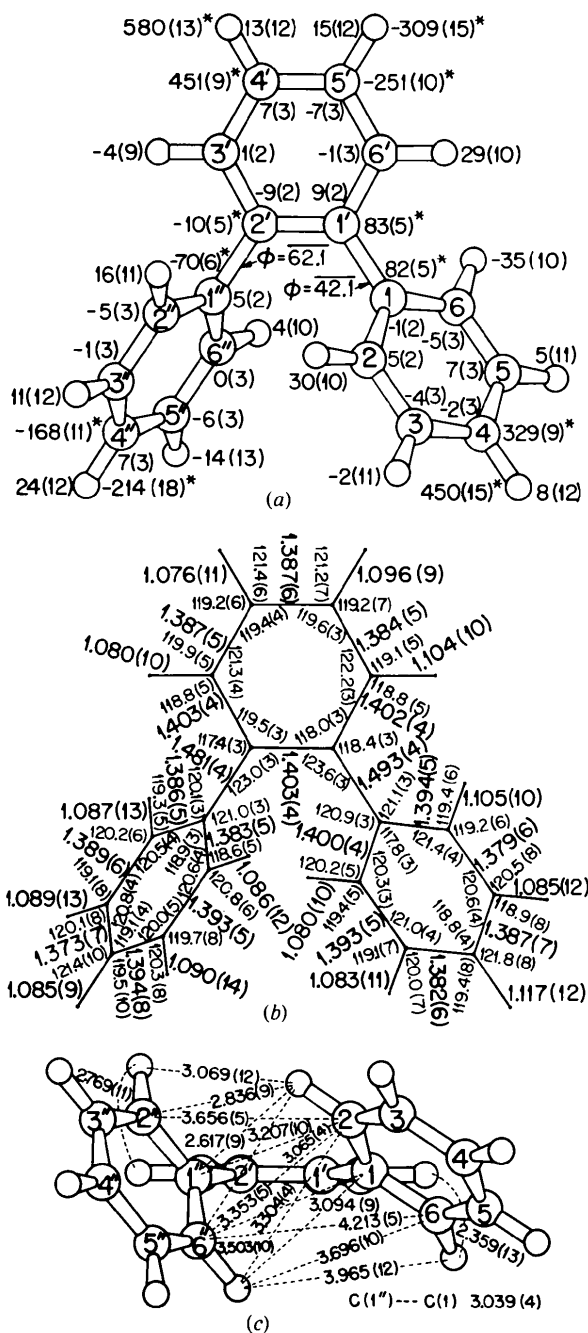


Fig. 2. Molecular structure of *o*-terphenyl. (a) View normal to the least-squares best plane through the middle ring, showing the twist angles  $\phi$  ( $^\circ$ ) about the inter-ring bonds and the deviations (in units of  $10^{-3} \text{ \AA}$ ) of atoms from the least-squares best planes through the rings. The C atoms are numbered by IUPAC rules. (b) Skeletal drawing showing all bond lengths ( $\text{\AA}$ ) and valence angles ( $^\circ$ ). (c) View in a direction normal to that of (a), showing the intramolecular nonbonded distances ( $\text{\AA}$ ) of interest in relation to the molecular conformation. The distances and angles have not been corrected for thermal motion. Numbers in parentheses give estimated standard errors calculated from the full least-squares covariance matrix. See text for further explanation.

atoms of each of the two overlapping biphenyl moieties of the molecule, a second out-of-plane deviation is also shown, marked with an asterisk. This is in each case for each moiety the deviation from the best plane for the ring to which the atom does *not* belong. Positive deviations are outward from the sides of the planes visible to the viewer of the top drawing.

As expected, there are a number of structural features of the *o*-terphenyl molecule that have their origin in the close proximity of the two bulky phenyl groups in *ortho* positions on the central ring. First, there are the twist angles,  $-42.1$  and  $-62.1^\circ$ , in the same sense about the inter-ring bonds  $C(1)-C(1')$  and  $C(1'')-C(2')$ . Some such cooperative twisting is necessary to minimize the repulsion between the two bulky phenyl groups. Other consequences of the overcrowding in the molecule are shown by the significant bending, in and out of the ring planes, at the ends of the inter-ring bonds. Thus, angles  $C(1)-C(1')-C(2')$  and  $C(1'')-C(2')-C(1')$  are opened to  $123.6(3)$  and  $123.0(3)^\circ$ . The axial atoms of the two terminal rings deviate considerably and in opposite directions from the central ring plane; so also do the atoms  $C(1')$ ,  $C(4')$ , and  $H(4')$  deviate considerably from the plane of C atoms 1-6 and atoms  $C(5')$  and  $H(5')$  from the plane of the C atoms 1''-6''. The torsion angle  $C(1)-C(1')-C(2')-C(1'')$  is  $-5.20^\circ$ . The angle between vectors  $C(1) \rightarrow C(4)$  and  $C(1') \rightarrow C(4')$  is  $172.5(1)^\circ$ ; that between  $C(1'') \rightarrow C(4'')$  and  $C(2') \rightarrow C(5')$  is  $175.1(1)^\circ$ .

Some of the intermolecular non-bonded distances shown in Fig. 2(c) are short enough to suggest considerable repulsion whatever reasonable van der Waals radii are assumed to apply. The three most significant displacements of H atoms from their ring planes, those for  $H(2)$ ,  $H(6)$ , and  $H(6')$ , are all for H atoms in rather close contact with another atom.

It might appear that so far as the molecule is concerned the energy would be lower if the molecule assumed the form with both twist angles at  $90^\circ$ . With this molecular conformation, which is actually the one deduced for the isolated molecule from electron-diffraction data (Karle & Brockway, 1944), the distances  $C(2) \cdots C(2'')$  and  $C(6) \cdots C(6'')$  would be  $\sim 3.8 \text{ \AA}$ , and the distances  $H(2) \cdots H(2'')$  and  $H(6) \cdots H(6'')$  would be  $\sim 3.2 \text{ \AA}$ . In the crystal the precise twist angles will depend upon the packing of the molecules as well as upon the interaction of the two neighboring phenyl groups within a molecule. An understanding of what determines the molecular conformation can be reached probably only through potential-energy calculations, not by superficial inspection of close contacts.

The object of this structure analysis was, in fact, to obtain data for testing the potential functions for hydrocarbons (Williams, 1970, 1974; Williams & Starr, 1977) which are required for predictions of conformations, packing, and energy. The effects of over-

crowding in *o*-terphenyl make the molecule and the crystal particularly interesting subjects for energy calculations, which are now being done with the program *WMIN* (Busing, 1971) by our colleague W. R. Busing in collaboration with us. Our accurate location of the H atoms, made possible by the use of neutron-diffraction data, is an advantage for these calculations, since a large fraction of the nonbonded intra- and intermolecular contacts involve the H atoms.

*Note added in proof:* After this paper had been refereed and provisionally accepted, the results of an X-ray crystal-structure analysis of *o*-terphenyl were published (Aikawa, Maruyama, Ohashi & Sasuda, 1978). The agreement between the two sets of bond lengths is poorer than one might wish, considering the apparent standard deviations of coordinates (very nearly the same for the two determinations). For example, the average  $|\Delta|$  for the C–C bond lengths is 0.014 Å, the r.m.s.  $\Delta$  is 0.018 Å, and the maximum  $|\Delta|$  is 0.035 Å. The corresponding measures of discrepancy for  $\Delta/\sigma_D$ , where  $\sigma_D$  is the standard error of  $\Delta$ , are 1.62, 2.00, and 3.95. A half-normal probability plot for the coordinates (Abrahams & Keve, 1971) suggests, however, that the pooled errors of the coordinates have been underestimated by a factor of  $\sim 2$ , so that the agreement, at least in relation to more realistic standard errors, may be considered to be better than at first sight.

#### References

- ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* **A27**, 157–165.
- AIKAWA, S., MARUYAMA, Y., OHASHI, Y. & SASUDA, Y. (1978). *Acta Cryst.* **B34**, 2901–2904.
- BUSING, W. R. (1971). Chemistry Division Annual Report, ORNL-4706, pp. 201–202. Oak Ridge National Laboratory, Tennessee.
- BUSING, W. R. & LEVY, H. A. (1957). **10**, 180–182.
- CLEWS, C. J. B. & LONSDALE, K. (1937). *Proc. R. Soc. London Ser. A*, **161**, 493–504.
- COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71–83.
- International Tables for X-ray Crystallography* (1962). Vol. III, p. 227. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1976). *ORTEP-II*. Report ORNL-5183 (3rd revision of ORNL-3794). Oak Ridge National Laboratory, Tennessee.
- KARLE, I. L. & BROCKWAY, L. O. (1944). *J. Am. Chem. Soc.* **66**, 1974–1979.
- KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.
- LANG, J. (1978). Private communication.
- LISENSKY, G. C., JOHNSON, C. K. & LEVY, H. A. (1976). *Acta Cryst.* **B32**, 2188–2197.
- MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1971). *MULTAN. A Computer Program for the Automatic Solution of Crystal Structures*, Univs. of York, England, and Louvain, Belgium.
- SHULL, C. G. (1972). Private communication.
- SPIRLET, M.-R. & BUSING, W. R. (1978). *Acta Cryst.* **B34**, 907–910.
- WILLIAMS, D. E. (1970). *Trans. Am. Crystallogr. Assoc.* **6**, 21–23.
- WILLIAMS, D. E. (1974). *Acta Cryst.* **A30**, 71–77.
- WILLIAMS, D. E. & STARR, T. L. (1977). *Comput. Chem.* **1**, 173–177.