There also exist some moderately short metal–metal distances between the columns: 3·5 Å in the **a** direction and 3·10 Å in the **c** direction. The previously mentioned bridging sulfur atoms also connect the columns in these directions. Thus Ta_2S might be a three-dimensional metal, either as a result of metal–metal interactions or because of the involvement of sulfur in the conduction process.

It is thus proposed that this structure, while highly unusual in detail, in broad outline is simply another example of delocalized directional bonding in a metal-rich sulfide. Bonding of this type has been proposed for lower sulfides of transition metals in general (Franzen, 1966).

According to a recent private communication from Professor F. Jellinek the Ta_2S phase has also been prepared in the Laboratory of Inorganic Chemistry, University of Groningen, by Dr G. A. Wiegers and Drs P. T. van Emmerik.

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The Crystal Structure of p,p'-Bitolyl

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Crystals of p,p'-bitolyl are monoclinic, space group $P2_1/c$, with $a=9·77$, $b=13·67$, $c=18·25$ Å, $\beta=118·3°$ and 8 molecules in the unit cell. Intensity data were collected from Weissenberg photographs about two crystal axes and measured with a microdensitometer. The crystal structure has been solved by the use of information from direct methods and Patterson syntheses. After least-squares refinement the final R index is 0·083. Both molecules in the asymmetric unit lie with their $H_3C\cdots CH_3$ axes nearly parallel to the b axis; the angle of twist between the phenyl rings assumes values of 36° and 40° for the two molecules. These values correspond to a definite minimum in a semi-empirical calculation of conformational energy in the crystal.

Introduction

The behaviour of the biphenyl molecule in different environments has been reviewed in a preceding paper (Casalone, Mariani, Mugnoli & Simonetta, 1968) where the theoretical geometry is also given, both for the gas phase and for 'model' crystals. The present work was undertaken to establish a comparison with the crystal structure of biphenyl, in which the coplanarity of the phenyl rings was first suggested by crystallo-graphic symmetry (Hengstenberg & Mark, 1929; Clark & Pickett, 1930, 1931), and more recently confirmed by two independent two-dimensional structure determinations (Trotter, 1961; Hargreaves & Rizvi, 1962).

Experimental

Crystals of p,p'-bitolyl (m. p. 121 °C) are white parallelepipeds elongated along **a**. The crystal data are collected in Table 1. The conventional cell leads to the

space group $P2_1/n$. Throughout this work, however, the alternative cell leading to space group $P2_1/c$ is used.

Table 1. Crystal data

p,p'-Bitolyl, $C_{14}H_{14}$, F.W. 182·27, monoclinic; $D_{méas}=$ 1·118 g.cm^{-3}, $D_{calc}=1·128$ g.cm^{-3}, $Z=8$; $F(000)=784$; $\lambda Cu\ K\alpha_1=1·5405$, $\lambda Cu\ K\alpha_2=1·5443$ Å.

	Conventional cell	Alternative cell used in this work
a	9·77±0·01 Å	9·77±0·01 Å
b	13·67±0·03	13·67±0·03
c	16·11±0·02	18·25±0·02
β	94·0 ±0·1°	118·3 ±0·1°
Cell volume	2146 Å^3	2146 Å^3
Systematic absences	$h0l$ for $h+l=2n+1$, $0k0$ for $k=2n+1$	$h0l$ for $l=2n+1$ $0k0$ for $k=2n+1$
Space group	$P2_1/n$	$P2_1/c$

The unit-cell parameters were obtained from a least-squares treatment of 66 measurements on zero-level Weissenberg photographs taken at room temperature around the crystallographic axes **a** and **b**, with Cu $K\alpha$ radiation. The uncertainties given in Table 1 are three times the corresponding estimated standard deviation increased to the next hundredth of an Å or to the next tenth of a degree.

For the determination of the structure, intensity data were collected from multiple-film equi-inclination Weissenberg photographs taken at room temperature. Layers 0–6 around **a** and 0–2 around **b** were obtained from nearly cube-shaped crystals whose thickness was about 0·4 mm. Copper $K\alpha$ radiation was used throughout. The intensities were estimated photometrically, by measuring the maximum blackening and the mean background for each reflexion, scaled together within the same layer by a method similar to that described by Rae (1965) and corrected for Lorentz, polarization and spot-size (Phillips, 1954) factors. No corrections either for absorption ($\mu Cu\ K\alpha=4·8$ cm^{-1}) or for extinction were made. An evaluation of the standard deviation for each individual observation was obtained from a statistical analysis (Gramaccioli & Mariani, 1967). The data belonging to different layers were scaled together according to the method proposed by Rollett & Sparks (1960), modified in order to account for the dependence of the weights upon the final scale factors (Hamilton, Rollett & Sparks, 1965; Duchamp, 1964). Of a total of 4908 possible reflexions available with Cu $K\alpha$ radiation, 3754 were collected, of which 2051 were too low to be measured; 352 were measured about both axes.

Structure determination and refinement

Some diffuse streaks parallel to **c*** were observed in the Weissenberg photographs, primarily along the rows 06l, 07l, 16l, 17l,39l, 3 10l, 49l, 4 10l, 59l, 5 10l, 69l, suggesting a distribution of vibrating atoms lying in a plane nearly parallel to the x,y plane (Lipson & Cochran, 1966). This fact is also in accord with the high in-

tensity observed for the 004 reflexion. However, the 200 reflexion is also predominant on the photographs; among the $h0l$ reflexions, 104 and 20$\bar{4}$ are very strong and, to a lesser extent, 40$\bar{4}$,408, 604,608, 80$\bar{8}$. Combining these pieces of information, one may reasonably presume that the two molecules in the asymmetric unit lie with their long axes nearly parallel to the b axis, at the same z value and probably at a separation of $a/2$ along x, the phenyl rings having different orientations.

An initial attempt to solve the structure was made by the use of direct methods. The intensities were brought to an approximately absolute scale by means of Wilson statistics and then normalized structure factors were evaluated as

$$|E_H|=|F_H|.\varepsilon^{-1/2}.\exp[B(\sin^2\theta)/\lambda^2].(\sum_{j=1}^{N}f_{j,H}^2)^{-1/2}$$

where, for space group $P2_1/c$, $\varepsilon=2$ for $h0l$ and $0k0$ reflexions and $\varepsilon=1$ otherwise. The mean values of some functions of $|E|$ are given in Table 2.

The presence of hypersymmetry is evident also from the $N(z)$ test (Howells, Phillips & Rogers, 1950) (see Fig. 1).

Table 2. Some functions of $|E|$

Function	Acentric	Centric	Experimental
$\langle|E|\rangle$	0·886	0·798	0·728
$\langle|E|^2\rangle$	1·000	1·000	0·981
$\langle|E^2-1|\rangle$	0·736	0·968	1·151

The sign determination was undertaken by application of the Σ_2 relationship for centrosymmetric crystals (Karle & Karle, 1966) to 254 reflexions with $|E| \geq 1·90$; at the end signs could be given to 206 reflexions as a function of one unknown symbol. Neither of the two corresponding E maps showed the orienta-
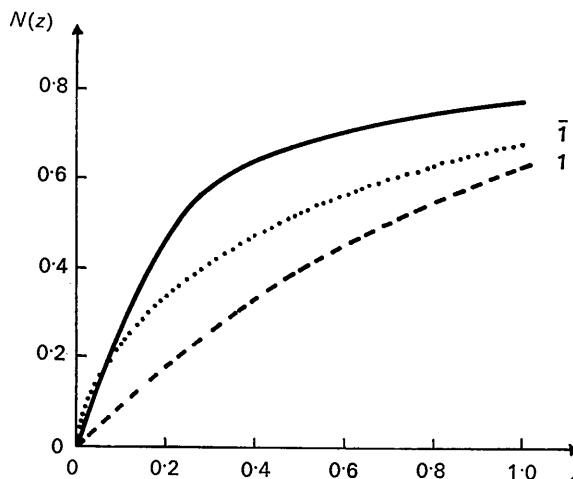

Fig. 1. $N(z)$ test for p,p'-bitolyl. The solid curve represents the experimental values.

Table 3. Observed and calculated structure factors

Items in order are k, l, $10|F_o|$, $10F_c$. Negative F_o values denote unobserved reflexions. Zero weight reflexions are marked with an asterisk.

H = 0

H = 1

H = 2

Table 3 (cont.)

[Table of structure factor data — dense multi-column numerical listing of h, k, l indices with observed and calculated structure factors, organized in sections H = 3, H = 4, H = 5, etc.]

tions of the phenyl rings clearly; however, it was apparent that the long axes of both molecules in the asymmetric unit were parallel to the *b* axis, and lay approximately at $x=0, z=\frac{1}{8}$ and $x=\frac{1}{2}$, $z=\frac{1}{8}$.

A three-dimensional sharpened Patterson synthesis computed in the neighbourhood of the origin and a subsequent $P(u0w)$ projection allowed us to confirm the positions of the molecular axes and to determine the

Table 3 (cont.)

orientations of the four rings. The x and z coordinates of all 28 carbon atoms were derived and led to an index $R = 0.35$ for the 140 observed $h0l$ reflexions. The y coordinates of the carbon atoms were derived by shifting the molecules along the b axis and varying the interval, Δy, between the mass centres of the two molecules in the asymmetric unit, while comparing the observed and calculated structure factors for the 59 $hk0$ reflexions for which sin $^2\theta/\lambda^2 \leq 0.15$.

The correct solution had the mass centres of the two molecules located approximately at $0,\frac{1}{4},\frac{1}{8}$ and at $\frac{1}{2},\frac{1}{4},\frac{1}{8}$. The corresponding structure factor calculation, performed on 256 hkl reflexions having sin$^2\theta/\lambda^2 \leq 0.10$, $|F_o|_{max} = 100$, $|F_c|_{min} = 10$, gave an index $R = 0.29$. Sixteen cycles of isotropic block-diagonal least-squares refinement, with gradually increasing numbers of data, lowered the R index to 0.13 for 893 hkl reflexions having sin$^2\theta/\lambda^2 \leq 0.20$, $|F_o|_{max} = 100$, $|F_c|_{min} = 6$.

Table 4. *The carbon atom parameters and their standard deviations*

All the values in this Table have been multiplied by 10^4. The temperature factor is in the form:

$$\exp\left[-(b_{11}h^2 + b_{12}hk + b_{13}hl + b_{22}k^2 + b_{23}kl + b_{33}l^2)\right].$$

	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
C(1)	58(8)	−1335(5)	1044(4)	313(11)	−32(11)	171(7)	65(4)	−18(6)	78(3)
C(2)	73(6)	−225(4)	1107(3)	211(7)	−19(8)	115(5)	54(3)	−12(4)	50(2)
C(3)	1373(6)	265(4)	1674(3)	180(7)	9(8)	90(5)	52(3)	8(4)	47(2)
C(4)	1414(5)	1265(4)	1761(3)	108(6)	−1(8)	33(5)	56(3)	7(4)	38(2)
C(5)	113(5)	1822(4)	1244(3)	133(6)	−12(7)	79(4)	55(3)	−1(4)	38(1)
C(6)	−1198(5)	1332(4)	675(3)	119(6)	−14(8)	32(5)	68(4)	−16(5)	40(2)
C(7)	−1215(6)	336(4)	600(3)	161(8)	−52(9)	61(6)	65(4)	−34(5)	57(2)
C(8)	122(4)	2903(4)	1331(2)	90(5)	−26(7)	42(4)	58(3)	−1(4)	30(1)
C(9)	893(5)	3352(4)	2084(3)	138(7)	−18(8)	48(5)	51(3)	−2(4)	41(2)
C(10)	853(5)	4363(4)	2161(3)	144(6)	−49(8)	93(5)	55(3)	−16(4)	57(2)
C(11)	57(5)	4947(4)	1474(3)	125(6)	−4(7)	114(5)	49(3)	2(5)	70(2)
C(12)	−719(6)	4497(4)	707(3)	146(7)	14(8)	82(5)	65(4)	16(5)	53(2)
C(13)	−697(5)	3491(4)	628(3)	120(6)	9(7)	53(5)	56(3)	10(4)	42(2)
C(14)	18(7)	6051(5)	1545(4)	230(8)	3(10)	205(7)	54(4)	−3(6)	118(3)
C(15)	5077(7)	1180(5)	1093(4)	262(9)	−8(11)	155(7)	62(4)	−5(6)	79(3)
C(16)	5008(5)	2274(4)	1149(3)	134(6)	−50(8)	70(6)	62(3)	−10(4)	43(2)
C(17)	6294(5)	2847(4)	1317(3)	137(6)	−26(9)	102(5)	73(4)	−32(5)	59(2)
C(18)	6238(5)	3840(4)	1360(3)	130(6)	−33(8)	81(4)	65(3)	−17(5)	50(2)
C(19)	4902(5)	4339(4)	1234(3)	122(5)	−5(7)	67(4)	54(3)	−0(4)	36(1)
C(20)	3617(5)	3753(4)	1082(3)	127(6)	−30(8)	79(4)	61(3)	8(4)	47(2)
C(21)	3666(5)	2758(4)	1023(3)	126(6)	−25(8)	66(5)	64(3)	7(4)	51(2)
C(22)	4843(5)	5403(4)	1274(3)	111(5)	−32(7)	56(4)	64(3)	−10(4)	33(1)
C(23)	5591(5)	5985(4)	938(3)	152(6)	−42(8)	87(5)	60(3)	−2(4)	47(2)
C(24)	5545(6)	6999(4)	987(3)	180(8)	−32(9)	57(6)	65(4)	−2(5)	42(2)
C(25)	4811(6)	7449(4)	1383(3)	137(7)	19(8)	21(6)	57(3)	6(5)	44(2)
C(26)	4077(6)	6883(5)	1714(3)	152(8)	33(9)	50(6)	72(4)	3(5)	52(2)
C(27)	4080(5)	5876(4)	1648(3)	140(6)	12(8)	83(4)	67(4)	1(4)	47(2)
C(28)	4814(7)	8570(5)	1449(4)	209(10)	4(11)	30(8)	66(4)	−6(6)	62(3)

The final refinement was accomplished by an anisotropic block-diagonal least-squares process. The quantity minimized was $\Sigma\, w(|F_o| - (|F_c/K|)^2$ with the weighting function $w = (A + B|KF_o| + C|KF_o|^2)^{-1}$; the parameters $A = 7$, $B = 1$, $C = 0\cdot02$ were chosen in order to give nearly constant mean values of $w(|KF_o| - |F_c|)^2$ as a function of F_o and of $\sin\theta/\lambda$. The number of parameters was 254: the coordinates and anisotropic thermal factors of the 28 carbon atoms, the overall temperature coefficient (Rollett, 1965) and the general scale factor. Of the 1703 measured intensities, 37 were omitted from the least-squares refinement as probably affected by extinction or other observational errors. In the structure factor calculations the benzenic hydrogen atoms were fixed, assuming a C–H distance of 1·08 Å. After a few cycles, when the R index for the observed reflexions was about 0·11, a three-dimensional difference Fourier synthesis allowed us to improve the positions of a few carbon and benzenic hydrogen atoms, and to recognize with some confidence eight of the twelve methyl hydrogen atoms (including at least one hydrogen atom for each methyl group). The positions of the remaining four hydrogen atoms were deduced from geometrical considerations.

The least-squares refinement was continued until the shifts in all parameters were lower than one-sixth of the corresponding standard deviation. At this final stage the reliability index, based on 1666 observed reflexions having non-zero weight, was $R = 0\cdot083$.

The observed and calculated structure factors are listed in Table 3, the final carbon atom parameters and their standard deviations in Table 4, and the hydrogen atom parameters in Table 5. The numbering of the atoms is shown in Fig. 2.

Table 5. *(Assumed) parameters of the hydrogen atoms*

	x	y	z	B
H(1)	0·240	−0·016	0·207	5·0
H(2)	0·245	0·162	0·222	5·0
H(3)	−0·224	0·175	0·028	5·0
H(4)	−0·225	−0·002	0·013	5·0
H(5)	0·156	0·291	0·263	5·0
H(6)	0·145	0·469	0·277	5·0
H(7)	−0·135	0·494	0·016	5·0
H(8)	−0·131	0·316	0·002	5·0
H(9)	0·737	0·250	0·142	5·0
H(10)	0·726	0·426	0·149	5·0
H(11)	0·256	0·410	0·101	5·0
H(12)	0·264	0·234	0·088	5·0
H(13)	0·621	0·565	0·064	5·0
H(14)	0·610	0·744	0·071	5·0
H(15)	0·350	0·722	0·203	5·0
H(16)	0·347	0·544	0·190	5·0
H(17)	−0·092	−0·164	0·109	5·5
H(18)	−0·012	−0·157	0·044	5·5
H(19)	0·108	−0·165	0·158	5·5
H(20)	0·061	0·623	0·222	5·5
H(21)	0·066	0·640	0·128	5·5
H(22)	−0·114	0·632	0·128	5·5
H(23)	0·436	0·083	0·131	5·5
H(24)	0·476	0·096	0·047	5·5
H(25)	0·630	0·095	0·150	5·5
H(26)	0·525	0·876	0·210	5·5
H(27)	0·545	0·888	0·116	5·5
H(28)	0·365	0·884	0·118	5·5

Accuracy of the results

The standard deviations in the coordinates, derived from the residuals and the diagonal elements of the inverse matrix of the final least-squares cycle, correspond to positional uncertainties between 0·005 and 0·008 Å. The corresponding standard deviations in the C–C bond lengths range from 0·006 to 0·010 Å. The standard deviations for the bond angles range from 0·4 to 0·6°.

Discussion

The first important difference with respect to the crystal structure of biphenyl is that all the molecules of p,p'-bitolyl in the crystal are packed with their long axes parallel to each other. A comparable crystallographic behaviour is found in p,p'-dimethoxybenzophenone (Karle, Hauptman, Karle & Wing, 1958) which crystallizes in space group $P2_1/a$ with eight molecules in the unit cell, all the molecules being disposed with the line connecting the methoxy oxygen atoms nearly parallel to the b axis. The other main difference from the crystal structure of biphenyl is the value of the angle of twist between the phenyl rings, here 36° and 40° for the two molecules in the asymmetric unit, in contrast with the assumption of near planarity of p,p'-bitolyl in the crystal, as inferred from the infrared spectra (Wilk, 1968). Our experimental values for p,p'-bitolyl lie near to the experimental (Almenningen & Bastiansen, 1958) and calculated (Casalone, Mariani, Mugnoli & Simonetta, 1968) values for the biphenyl molecule in the gas phase.

The difference in behaviour in the solid phases between biphenyl and p,p'-bitolyl comes presumably from the different environments in the two crystals. It has

been shown (Casalone, Mariani, Mugnoli & Simonetta, 1968) that intermolecular forces lead to a planar conformation in the case of biphenyl. Analogous calculations have now been performed for p,p'-bitolyl, following the same principles. To keep the calculation to a reasonable size a model crystal was used with regular phenyl rings and average bond distances, with the centre of mass of each molecule in the experimental position and the molecular axes parallel to the b axis. Independent rotations of each ring around the molecular axes have been allowed. For each geometry the energy of the model crystal was obtained by summing the energies of the two independent isolated molecules, which are a function of the angle of twist between the rings in a molecule, and the intermolecular interactions, which have been included up to distances of 5·8, 5, 4·2 Å for $C \cdots C$, $C \cdots H$, $H \cdots H$ pairs respectively. The results of this calculation are shown in Fig. 4. It is gratifying that the absolute minimum of energy corresponds to the same orientations of the rings as found experimentally.

A similar angle of twist ($\theta = 33°$) is found in 4,4'-dinitrodiphenyl (Boonstra, 1963), while the molecule

Table 6. *Average values and r.m.s. deviations for 'chemically equivalent' bond lengths (Å) and angles (°) in the two molecules (see text)*

Type of bond or angle	Multiplicity	Mean value	r.m.s. deviation
C(1)–C(2)	4	1·520	
C(3)–C(4)	8	1·378	0·011
C(2)–C(3)	16	1·385	0·012
C(5)–C(8)	2	1·473	
C(4)–C(5)–C(6)	8	117·5	1·0
C(2)–C(3)–C(4)	16	121·2	0·9

Table 7. *Some least-squares planes*

The coefficients q_i are the direction cosines relative to the crystallographic axes a, b and c. All the atoms were given equal weights. In the lower part of the Table, the deviations (in Å) are given. Plane I is the mean plane through the twelve atoms lying along the two molecular axes (see text). An asterisk identifies the atoms defining the other planes.

Plane	q_1	q_2	q_3	D (Å)
I	0·0560	−0·0651	0·8508	1·798
II	−0·7340	−0·0734	0·9424	1·878
III	0·9904	0·0762	−0·5708	−0·965
IV	−0·1908	−0·0663	0·9528	0·853
V	0·4877	−0·0368	0·5369	3·274

	II	III		IV	V
C(1)	0·009*	−0·206	C(15)	−0·006*	0·157
C(2)	−0·004*	−0·141	C(16)	0·006*	0·124
C(3)	−0·011*		C(17)	0·006*	
C(4)	0·009*		C(18)	0·001*	
C(5)	−0·003*	−0·032	C(19)	−0·014*	0·053
C(6)	0·008*		C(20)	0·014*	
C(7)	−0·009*		C(21)	−0·007*	
C(8)	0·032	−0·002*	C(22)	−0·030	0·010*
C(9)		0·007*	C(23)		0·008*
C(10)		−0·007*	C(24)		−0·017*
C(11)	0·120	−0·001*	C(25)	−0·020	−0·001*
C(12)		0·001*	C(26)		0·002*
C(13)		−0·001*	C(27)		−0·011*
C(14)	0·159	0·003*	C(28)	−0·007	0·008*

of 4,4'-dihydroxydiphenyl, as biphenyl itself, displays crystallographic symmetry $\bar{1}$ (Wallwork & Powell,

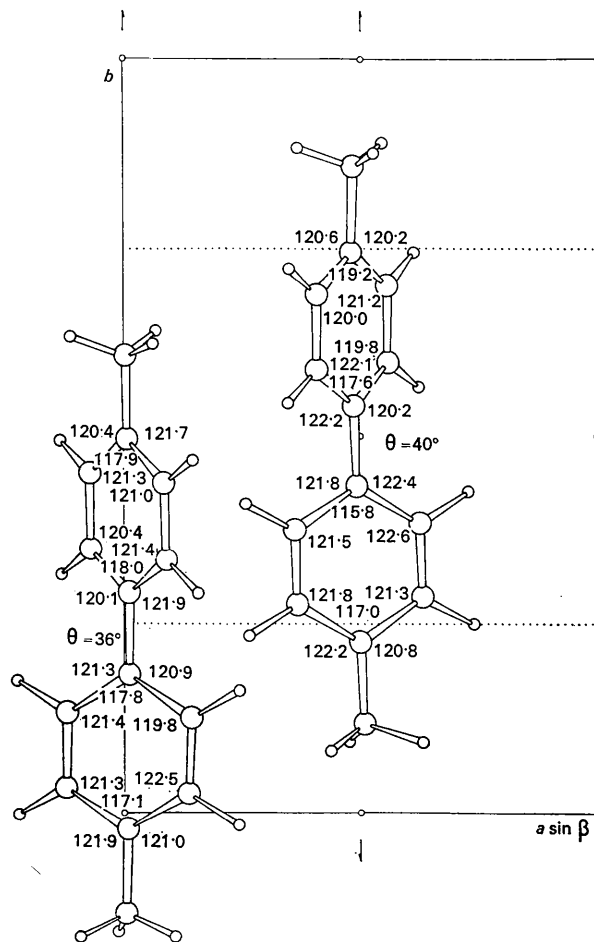Fig. 2. The asymmetric unit projected down the c axis, showing the numbering of atoms and the bond distances.

Fig. 3. Bond angles and angles of twist, θ.

Table 8. *Magnitudes and direction cosines, relative to the crystallographic axes, of the principal axes of the thermal ellipsoids*

	B_i	$q_i{}^a$	$q_i{}^b$	$q_i{}^c$		B_i	$q_i{}^a$	$q_i{}^b$	$q_i{}^c$		B_i	$q_i{}^a$	$q_i{}^b$	$q_i{}^c$		B_i	$q_i{}^a$	$q_i{}^b$	$q_i{}^c$
C(1)	9.49	0.753	-0.178	0.201	C(8)	4.59	0.381	-0.922	-0.244	C(15)	8.34	0.375	-0.063	0.637	C(22)	5.10	0.311	-0.921	0.058
	7.24	0.656	0.117	-0.968		3.26	0.422	0.242	-0.969		6.95	0.926	-0.010	-0.771		3.53	0.587	-0.007	-0.991
	4.64	0.058	0.977	0.152		2.46	0.823	0.303	0.033		4.61	0.032	0.998	0.033		2.97	0.748	0.388	0.119
C(2)	6.40	0.767	-0.212	0.169	C(9)	5.41	0.841	-0.196	-0.842	C(16)	5.54	0.566	-0.799	-0.089	C(23)	5.51	0.654	-0.726	-0.123
	4.60	0.637	0.358	-0.903		4.01	0.242	-0.697	0.480		4.53	0.358	0.015	-0.992		4.77	0.118	-0.179	-0.916
	3.86	0.072	-0.909	-0.395		3.41	0.483	0.690	0.245		3.08	0.743	0.601	-0.093		3.31	0.747	0.664	-0.381
C(3)	5.36	0.892	0.132	-0.041	C(10)	6.14	0.052	-0.355	0.797	C(17)	7.19	0.019	0.629	-0.693	C(24)	6.64	0.897	-0.399	-0.591
	4.84	0.453	-0.285	-0.959		4.89	0.740	-0.614	-0.593		4.35	0.012	0.777	0.548		4.67	0.250	0.811	-0.584
	3.80	0.012	0.949	-0.282		3.01	0.670	0.705	-0.115		3.52	1.000	-0.021	-0.468		4.04	0.364	0.427	0.557
C(4)	5.23	0.685	-0.337	-0.894	C(11)	7.30	0.077	-0.027	-0.914	C(18)	5.77	0.074	-0.651	0.630	C(25)	7.08	0.823	0.057	-0.888
	4.06	0.303	0.938	-0.291		3.69	0.194	-0.980	-0.055		4.59	0.507	-0.628	-0.760		4.43	0.158	0.933	0.210
	2.94	0.663	-0.082	0.341		2.95	0.978	0.196	-0.402		3.38	0.859	0.427	-0.158		3.13	0.546	-0.356	0.409
C(5)	4.34	0.505	-0.679	0.230	C(12)	5.94	0.185	-0.520	-0.822	C(19)	4.08	0.208	-0.973	-0.007	C(26)	7.07	0.753	0.306	-0.870
	3.97	0.170	0.684	0.544		4.54	0.636	0.710	-0.567		3.74	0.315	0.168	0.673		5.48	0.050	0.856	0.430
	3.25	0.846	0.268	-0.807		4.15	0.749	-0.475	0.052		3.40	0.926	0.161	-0.739		3.86	0.656	-0.417	0.243
C(6)	5.89	0.586	0.540	-0.809	C(13)	5.09	0.514	-0.400	-0.912	C(20)	5.42	0.423	-0.707	-0.700	C(27)	5.08	0.244	0.941	0.091
	4.95	0.578	-0.801	-0.411		4.17	0.531	0.843	-0.326		4.64	0.319	-0.470	0.574		4.88	0.096	0.217	-0.901
	3.01	0.568	0.258	0.419		3.40	0.674	-0.360	0.249		2.99	0.848	0.529	-0.425		3.86	0.965	-0.259	-0.425
C(7)	7.37	0.505	0.346	-0.936	C(14)	12.18	0.019	0.017	-0.889	C(21)	5.99	0.498	-0.517	-0.849	C(28)	10.42	0.844	0.060	-0.869
	5.96	0.744	-0.640	-0.181		5.39	0.994	0.108	-0.453		4.71	0.164	-0.732	0.504		4.99	0.304	-0.872	0.194
	3.20	0.439	0.686	0.303		3.99	0.109	-0.994	-0.065		3.41	0.851	0.444	-0.157		4.80	0.441	0.486	0.455

1951; Farag & Kader, 1960). A recent investigation (Neronova, 1968) gives a twist of 62° for decafluoro-biphenyl. This large value can be explained on the basis of the strong interactions between the fluorine atoms in *ortho* positions.

Bond distances and angles are shown in Figs. 2 and 3. All these values are uncorrected for librational effects. To allow for a possible quinoid character, two groups of benzenic C–C bond distances have been considered: those parallel to, and those inclined with respect to, the axes of the two molecules. In Table 6 the average values with root mean square deviations are reported for 'chemically equivalent' bond lengths and angles in the two molecules.

All but one of the intermolecular distances are longer than the corresponding van der Waals distances, as computed with $r_C = 1\cdot6$ and $r_H = 1\cdot2$ Å: there is only one short $H\cdots H$ interaction ($2\cdot3$ Å) between two benzenic hydrogen atoms.

The average planes have been determined by the method of Schomaker, Waser, Marsh & Bergman (1959). The mean plane I through the axes of the two molecules in the asymmetric unit (see Table 7) lies approximately perpendicular to c^*, as deduced from the Weissenberg photographs. With respect to this plane, the maximum displacement of any of the twelve atoms is $0\cdot07$ Å. The mean planes for each molecule were first computed for ten atoms, including one phenyl ring, the bonded methyl carbon atom and the three other carbon atoms along the molecular axis. This led, however, to deviations as large as $0\cdot05$ Å for the extreme atoms, indicating an out-of-plane bending of the molecular axes as observed for 4,4'-diamino-3,3'-dimethylbiphenyl by Chawdhury, Hargreaves & Sullivan (1968). The seven-atom mean planes (II, III, IV and V in Table 7) were then computed, considering one phenyl ring and the bonded methyl carbon atom for each. For three of these four cases the distances
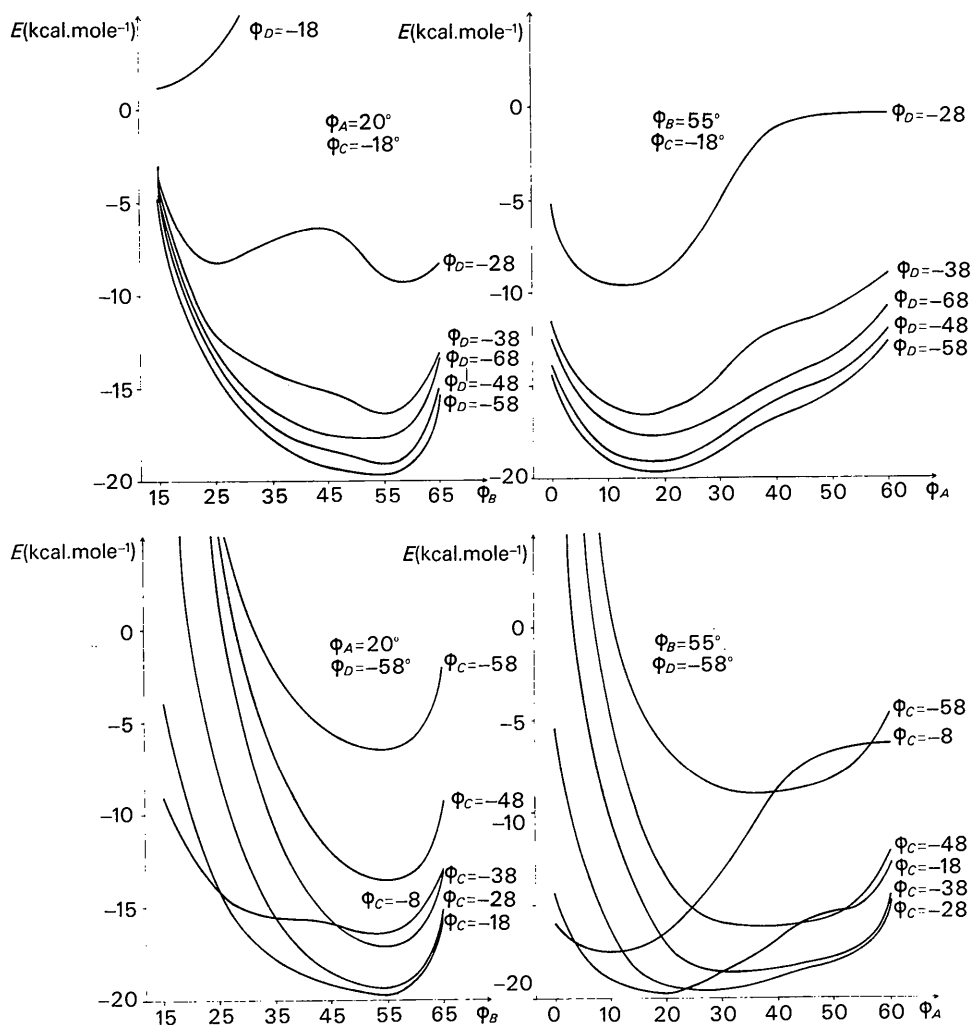

Fig. 4. Total energy in the model crystals as a function of the dihedral angles φ_A, φ_B, φ_C, φ_D between the planes of the phenyl rings (see Fig. 3) and the plane orthogonal to the c axis. The experimental values are $\varphi_A = 20°$, $\varphi_B = 55°$, $\varphi_C = -18°$, $\varphi_D = -58°$.

from the plane of the three remaining axial carbon atoms increases linearly on going away from the ring; the maximum amount of this out-of-plane bending is 2·3° (plane III). The maximum displacement of the atoms defining the mean planes is less than 0·02 Å.

The lengths and direction cosines of the principal axes of thermal vibration are given in Table 8. The anisotropy is particularly evident for the methyl carbon atoms.

A study of the possible rotation of the methyl groups around their axes was made by evaluation of the H·· H interactions using Bartell's (1960) formula and considering only the atoms lying at a distance $r \le r_0$ from the methyl hydrogen atoms, where r_0 is the abscissa of the minimum in the curve. The maximum height of the resulting barriers was only 22 cal.mole^{-1}. However, this fact cannot be taken as proof that the freedom of rotation of methyl groups shown in isolated molecules of methylbenzenes (Woolfenden & Grant, 1966) is maintained in our crystal; a more sophisticated calculation allowing C···H and H···H interactions both for the attractive and repulsive region might lead to a significant barrier height.

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Least-Squares Weighting Schemes for Diffractometer-Collected Data. IV. The Effect of Random Errors in the Form Factors Resulting from Bonding

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An analysis is made of the random errors that are encountered in a diffractometer experiment. These are the result of counting statistics, random setting errors and random errors resulting from errors in the form factors caused by bonding between atoms. For the all-light-atom example considered this latter error is of the order of 3%. A schematic technique for obtaining absolute weights is indicated.

Introduction

Analysis of the weighting function for least-squares refinement derived on the basis of counting statistics and random instrumental setting errors for a diffractometer experiment leads to an expression

$$1/w(\mathbf{h}) = \sigma_1^2(\mathbf{h}) + \sigma_2^2(\mathbf{h})$$