582. *Molecular Polarisability. The Conformations of Certain Amides as Solutes in Dioxan*

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Dipole moments and molar Kerr constants are reported for formamide (3·85 D and 284 × 10^{-12}), *N*-methylformamide (3·84 D and 210 × 10^{-12}), *NN*-dimethylformamide (3·91 D and 417 × 10^{-12}), *N*-t-butylformamide (3·94 D and 336 × 10^{-12}), *NN*-diphenylformamide (3·44 D and 406 × 10^{-12}), acetamide (3·87 D and 257 × 10^{-12}), *N*-t-butylacetamide (3·85 D and 195 × 10^{-12}), and benzamide (3·76 D and 234 × 10^{-12}) as solutes in dioxan at 25°. The data are analysed to indicate that (a) the *trans*-isomer abundances for *N*-methylformamide and *N*-t-butylformamide are 90 and *ca.* 71%, respectively, (b) benzamide in dioxan is non-planar, the dihedral angle between the benzene ring and the plane of the amide group being 37° ± 5°, and (c) the preferred conformation of *NN*-diphenylformamide is attained by rotations (in the same sense) of both phenyl groups through 52° ± 5° from a theoretical planar model.

This Paper is concerned with the experimental determination of the dipole moments and molar Kerr constants of a number of acid amides, and with the analysis of such data to yield information on the configurations of these molecules as solutes at high dilution in dioxan.

Table 1

Incremental Kerr constants, dielectic constants, densities, and refractive indices for solutions in dioxan at 25°

Formamide

10^5w_2 ...	515	583	753	850	1081	1258	1570	2083
$10^7\Delta B$ ...	0·180	0·203	0·264	0·306	0·410	0·515	0·629	0·818
ε^{25}	2·4195	2·4480	2·5144	—	2·6466	—	2·8471	3·0701

whence $\Sigma 10^7\Delta B/\Sigma w_2 = 38{\cdot}2$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 40{\cdot}9$

10^5w_2 ...	1215	1386	1510	2184	2829	3853
$10^4\Delta n$ ...	—	4	—	6	8	11
d_4^{25}	1·02961	1·02984	1·03000	1·03093	1·03174	1·03310

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}028$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}133$

N-*Methylformamide*

10^5w_2 ...	342	430	515	545	618	771	849	974
$10^7\Delta B$ ...	0·088	0·106	0·129	0·146	0·170	0·221	0·262	0·289

whence $10^7\Delta B = 21{\cdot}8w_2 + 889w_2^2$

10^5w_2 ...	375	505	567	824	1074	1292	1769	2075
ε^{25}	2·3238	2·3818	2·3903	2·4820	2·5745	2·6851	2·8610	2·9920

whence $\Delta\varepsilon = 30{\cdot}9_5w_2 + 333w_2^2$

10^5w_2 ...	1137	1554	2109	3232	6691
$10^4\Delta n$ ...	—	—	2	3	7
d_4^{25}	1·02793	1·02791	1·02788	1·02777	1·02753

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}010$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}006_7$

TABLE 1 (*Continued*)

NN-*Dimethylformamide*

10^5w_2 ...	472	485	704	780	1035	1287	1751
$10^7\Delta B$ ...	0·149	—	0·248	0·253	0·347	0·428	0·638
ε^{25}.........	—	2·3351	—	2·4114	2·4751	2·5426	2·6645

whence $\Sigma 10^7\Delta B/\Sigma w_2 = 34{\cdot}2$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 25{\cdot}9$

10^5w_2 ...	980	1572	1947	2606	3527
d_4^{25}	1·02704	1·02649	1·02611	1·02552	1·02459

whence $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}096$; $\Delta n =$ *ca.* 0 for concentrations up to $w_2 = 0{\cdot}03$

N-*t*-*Butylformamide*

10^6w_2 ...	2543	3551	4404	5510
$10^7\Delta B$ ...	0·0527	0·0672	0·0919	0·1076

whence $\Sigma 10^7\Delta B/\Sigma w_2 = 20{\cdot}0$

10^5w_2......	2700	5908	10,885
$10^4\Delta n$ ...	3	6	13

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}011$

10^5w_2 ...	519	698	976	1175	1279	1720	2138	2215
ε^{25}.........	2·3074	2·3411	2·3952	2·4315	2·4568	2·5345	2·6160	2·6352
d_4^{25}	1·02726	1·02706	1·02666	—	1·02615	1·02560	—	1·02491

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 19{\cdot}1$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}140$

NN-*Diphenylformamide*

10^5w_2 ...	204	375	508	594	697
$10^7\Delta B$ ...	0·0252	0·0468	0·0623	0·0700	0·0870

whence $\Sigma 10^7\Delta B/\Sigma w_2 = 12{\cdot}3$

10^5w_2 ...	339	609	910	1315	1733	2679
$10^4\Delta n$ ...	—	10	—	21	29	44
ε^{25}.........	2·2263	2·2565	2·2803	2·3122	2·3454	2·4209
d_4^{25}	1·02840	—	1·02906	1·02954	1·02995	1·03098

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}164$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 7{\cdot}88$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}114$

Acetamide

10^5w_2 ...	431	523	644	733	851	1619	2060
$10^7\Delta B$ ...	0·108	0·127	0·172	0·182	0·240	0·417	0·566

whence $\Sigma 10^7\Delta B/\Sigma w_2 = 26{\cdot}4$

10^5w_2 ...	1250	1715	1973	2352	2766
$10^4\Delta n$ ...	1	1	2	2	2
d_4^{25}	1·02844	1·02859	1·02870	1·02880	1·02891

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}008$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}034$

10^5w_2 ...	532	801	1124	1616	2014
ε^{25}.........	2·3752	2·4583	2·5582	2·7164	2·8466

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 31{\cdot}4$

N-*t*-*Butylacetamide*

10^5w_2 ...	558	577	772	992	1096	1405	2053
$10^7\Delta B$ ...	0·060	0·066	0·090	0·125	0·137	0·186	0·295

whence $10^7\Delta B = 10{\cdot}4w_2 + 196w_2^2$

10^5w_2...	3058	3917	9090
$10^4\Delta n$...	4	5	13

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}014$

10^5w_2 ...	727	941	1138	1498	1986	2436	2794	3058
ε^{25}.........	2·3301	2·3651	2·3997	2·4637	2·5536	2·6426	2·7109	2·7689
d_4^{25}	1·02695	—	1·02624	1·02582	1·02502	1·02441	—	1·02341

whence $\Delta\varepsilon = 15{\cdot}9w_2 + 78{\cdot}2w_2^2$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}149$

Benzamide

10^5w_2 ...	550	830	1037	1205	1405	1552
$10^7\Delta B$ ...	0·062	0·096	0·125	0·144	0·170	0·177

whence $\Sigma 10^7\Delta B/\Sigma w_2 = 11{\cdot}8$

10^5w_2 ...	684	1059	1883	2571
$10^4\Delta n$ ...	10	15	29	39
ε^{25}.........	—	2·3657	2·4914	2·5925
d_4^{25}	1·02910	1·02960	1·03080	1·03169

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}150$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 14{\cdot}9$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}147$

EXPERIMENTAL

Materials, Apparatus, etc.—*N*-t-Butylformamide, prepared by the addition of a solution of sulphuric acid in acetic acid to a mixture [1] of t-butyl alcohol, sodium cyanide, and acetic acid, had b. p. 200—202°. *N*-t-Butylacetamide, prepared by passing gaseous isobutene (generated from a heated t-butyl alcohol–conc. sulphuric acid mixture) into a solution [2] of acetonitrile, acetic acid, and sulphuric acid, had m. p. 98° (from hexane). The other solutes were commercial samples which on purification gave: formamide, b. p. 79°/6 mm.; *N*-methylformamide, b. p. 82°/10 mm.; *NN*-dimethylformamide, b. p. 76°/39 mm.; *NN*-diphenylformamide, m. p. 73·5°; acetamide, m. p. 80°; benzamide, m. p. 128°.

Apparatus, techniques, symbols used, and methods of calculation have been described before.[3-5] Observations are recorded in Table 1 and results summarised in Table 2. The quantities $\Delta\varepsilon$, Δd, Δn, and ΔB are the differences found between the dielectric constants, densities, refractive indices, and Kerr constants, respectively, of the solvent and of solutions containing weight fractions w_2 of solute. The following data apply at 25° to dioxan: $\varepsilon_1 = 2{\cdot}2090$; $d_1 = 1{\cdot}0280$; $(n_D)_1 = 1{\cdot}4202$; $10^7B_1 = 0{\cdot}068$; $10^{1}{}_{s}{}^{2}K_1 = 0{\cdot}0116$.

TABLE 2

Dielectric polarisations, dipole moments, and molar Kerr constants (from observations on solutions in dioxan at 25°)

Solute	$\alpha\varepsilon_1$	β	γ	δ	${}_{\infty}P_2$ (c.c.)	R_D (c.c.)	μ (D) *	$10^{12}{}_{\infty}({}_mK_2)$ ‡
Formamide	40·9	0·129	0·02	562	314	10·3	3·85	284
N-Methylformamide	$30{\cdot}9_5$ †	−0·007	0·01	321 †	317	14·9	3·84	210
NN-Dimethylformamide	25·9	−0·094	0	503	334	19·7	3·91	417
N-t-Butylformamide	19·1	−0·136	0·01	294	350	28·9	3·94	336
NN-Diphenylformamide	7·88	0·111	0·12	180	305	59·8	3·44	406
Acetamide	31·4	0·033	0·01	388	321	14·3	3·87	257
N-t-Butylacetamide	15·9 †	−0·145	0·01	153 †	337	33·2	3·85	195
Benzamide	14·9	0·143	0·11	173	326	34·9	3·76	234

* Calculated assuming ${}_DP = 1{\cdot}05R_D$; uncertainty in μ *ca.* ±0·03 D. † Variation of ε_{12} or B_{12} with w_2 was non-linear over the concentration range studied; the experimental data ($\Delta\varepsilon$ or ΔB) were fitted to a regression equation of the form $\Delta\varepsilon = aw_2 + bw_2^2$, and subsequent extrapolation to $w_2 = 0$ resulted in the coefficients $\alpha\varepsilon_1$ or δ here recorded. ‡ Uncertainty in ${}_{\infty}({}_mK_2)$ values is estimated at ±5%.

Previous Measurements.—McClellan [6] lists the following values for dipole moments (D) in dioxan: formamide, 3·0,[7] 3·86;[8] acetamide, 3·90,[8] 3·6,[9] 3·92;[10] benzamide, 3·84,[8] 3·6,[9] 3·80,[11] 3·88.[12] In addition, the following values (in dioxan) were recorded by Lee and Kumler:[13] *NN*-dimethylformamide, 3·95; acetamide, 3·70. The vapour phase dipole moments, recently reported [14] for *N*-methylformamide (3·82), *NN*-dimethylformamide (3·80), and acetamide (3·75), are similar to the values (in Table 2) now derived by extrapolation to infinite dilution in dioxan.

DISCUSSION

Bond and Group Polarisabilities.—Initially we examine the degree of applicability of bond polarisability data previously recorded [15] [b_L(H–N) = 0·50, b_T(H–N) = b_V(H–N) =

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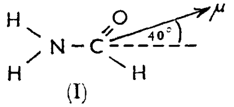
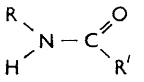
[15] M. J. Aroney, R. J. W. Le Fèvre, and A. N. Singh, *J.*, 1963, 5111.

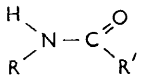
0·83; b_L(C–N) = 0·57, b_T(C–N) = b_V(C–N) = 0·69; b_L(C=O) = 2·30, b_T(C=O) = 1·40, b_V(C=O) = 0·46; b_L(C–H) = b_T(C–H) = b_V(C–H) = 0·64] * to the calculation of molecular parameters for the amides. For a planar model (I) of formamide,[16] the polarisability tensor is specified, by addition [5] of the component bond ellipsoids, as: b_1(calc.) = 4·87, b_2(calc.) = 4·04, b_3(calc.) = 3·45, where b_1 and b_2 are located in the plane of symmetry such that the b_1 axis makes an angle of 50° with N–C and 10° with C=O. If the permanent electric moment (3·85 D) acts at 40° to the N–C bond (found from Stark effect measurements by Kurland and Bright Wilson [16]), then the vector components along the principal axes are: $\mu_1 = 3{\cdot}79$ D, $\mu_2 = 0{\cdot}67$ D, and $\mu_3 = 0$. Substitution of these values in equations (1)—(3) leads to a predicted molar Kerr constant of 178 × 10^{-12} (assuming ${}_{\mathrm{D}}P/{}_{\mathrm{E}}P = 1{\cdot}1$) which is considerably lower than that observed (284 × 10^{-12}). Clearly the H–N, C–N, and C=O bond polarisabilities listed above, which were derived from simple molecules, cannot be used to specify the highly resonating amide group $[{>}N{-}\overset{|}{C}{=}O \;\; {>}\overset{+}{N}{=}\overset{|}{C}{-}O^{-}]$.



(I)



(II) *trans*



(III) *cis*

$$ {}_{m}K = 2\pi N(\theta_1 + \theta_2)/9 \qquad (1) $$

$$ \theta_1 = {}_{\mathrm{D}}P[(b_1 - b_2)^2 + (b_2 - b_3)^2 + (b_3 - b_1)^2]/45kT{}_{\mathrm{E}}P \qquad (2) $$

$$ \theta_2 = [(b_1 - b_2)(\mu_1^2 - \mu_2^2) + (b_2 - b_3)(\mu_2^2 - \mu_3^2) + (b_3 - b_1)(\mu_3^2 - \mu_1^2)]/45k^2T^2 \qquad (3) $$

The quantity $(\theta_1 + \theta_2)$ is calculable for formamide from the observed molar Kerr constant [using equation (1)] as 67·5 × 10^{-35}. Since μ(obs.) is large, then $\theta_1 \leqslant \theta_2$, and as $(\theta_1 + \theta_2)$, and hence θ_2, are very great and positive, it follows that the maximum polarisability axis must be located very near to the dipole-moment direction. If we make the reasonable approximations that $\theta_1 = 0$ and $\mu_1 = \mu$(obs.), equations (1), (3), and (4) can be solved, to yield values of b_1 (=5·04) and $(b_2 + b_3)$ (=6·60).

$$ {}_{\mathrm{E}}P = 0{\cdot}95R_{\mathrm{D}} = 4\pi N(b_1 + b_2 + b_3)/9 \qquad (4) $$

Similar considerations can safely be applied to each of the aliphatic amides of Table 2. The estimates of b_1 and of $(b_2 + b_3)$ thus obtained are listed in Table 3. Further, the observed moments for these molecules are virtually constant (all lie within the range 3·89 ± 0·05 D), so we will assume that, in each case, μ(obs.), and hence b_1, are located as shown in (I) for formamide.

TABLE 3

Polarisability semi-axes

Compound	b_1	$(b_2 + b_3)$	Compound	b_1	$(b_2 + b_3)$
Formamide	5·04	6·60	*N*-t-Butylformamide	12·16	20·42
N-Methylformamide	6·49	10·40	Acetamide	6·42	9·74
NN-Dimethylformamide	9·06	13·18	*N*-t-Butylacetamide	13·31	24·24

La Planche and Rogers [17] recently showed from an n.m.r. spectral study of *N*-monosubstituted amides, that *N*-t-butylacetamide, unlike the corresponding formamide, exists exclusively as the *trans*-configuration (II). We accept this in the following discussion. If, then, the C–C and C–H link polarisability contributions [15] [b_L(C–C) = 0·99, b_T(C–C) = b_V(C–C) = 0·27] of the t-butyl group are subtracted from b_1(*N*-t-butylacetamide) we are

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* Polarisability semi-axes of bonds b_L, b_T, or b_V, or of molecules, b_1, b_2, or b_3, are quoted throughout in 10^{-24} c.c. (Å^3) units.

[16] R. J. Kurland and E. Bright Wilson, *J. Chem. Phys.*, 1957, **27**, 585.

[17] L. A. La Planche and M. T. Rogers, *J. Amer. Chem. Soc.*, 1964, **86**, 337.

left with b_1[C(*trans*)·NH·CO·CH$_3$] = 5·81. Comparison of this quantity with b_1(acetamide) shows that substitution of an N–H by an N–C link wholly in the *trans*-position results in an incremental change in b_1 of −0·61. A similar substitution in the *cis*-position leads to a change in b_1 of +0·79 [from b_1(*NN*-dimethylformamide), b_1(formamide), and Δb_1(*trans*) = −0·61]. It is possible, on this basis, to predict, from b_1(formamide), the theoretical values of b_1(*trans*) and b_1(*cis*) for *N*-methylformamide and for *N*-t-butylformamide. The calculations are summarised in Table 4. It should be noted that in all cases considered the amide group is assumed to be planar. We thus conclude that, in dioxan solution, each of these molecules exist in both the *cis*- and *trans*-configurations, with the latter predominant. The *trans*-isomer abundances recorded in Table 4 agree reasonably with those (92% for *N*-methylformamide and 82% for *N*-t-butylformamide) given by La Planche and Rogers.[17]

TABLE 4

	Compound	b_1(*trans*)	[b_2(*trans*) + b_3(*trans*)]	$_{\rm m}K$(*trans*)
(i)	*N*-Methylformamide	6·35	10·54	176 × 10^{-12}
(ii)	*N*-t-Butylformamide	11·93	20·65	275

	b_1(*cis*)	[b_2(*cis*) + b_3(*cis*)]	$_{\rm m}K$(*cis*)	$_{\rm m}K$(obs.)	% *trans*
(i)	7·75	9·14	518 × 10^{-12}	210 × 10^{-12}	90
(ii)	12·74	19·84	483	336	*ca.* 71 *

* b_1(*trans*) and b_1(*cis*) are not sufficiently divergent to allow a precise estimate of the *trans* : *cis* ratio.

Benzamide.—Specification of the molecular polarisability tensor can be effected by additivity of the component C_6H_5 and $H_2N·CO·C$ group semi-axes. In the calculations, the following data were used [for C_6H_5 (ref. 15) and $H_2N·CO·C$,* respectively]: b_1, 10·56 and 4·50; b_2, 10·56 and 2·95; b_3, 6·72 and 2·95.

TABLE 5

Polarisabilities and molar Kerr constants calculated for conformations of benzamide

		Direction cosines with			
ϕ	b_i (calc.)	X	Y	Z	$10^{12}{}_{\rm m}K$ (calc.)
0°	b_1 = 15·06	+0·771	+0·637	0	+554
	b_2 = 13·51	+0·637	−0·771	0	
	b_3 = 9·67	0	0	+1	
26°	b_1 = 13·51	+0·627	−0·775	+0·076	+383
	b_2 = 14·85	+0·721	+0·615	+0·318	
	b_3 = 9·89	−0·293	−0·144	+0·945	
36°	b_1 = 13·51	+0·626	−0·772	+0·113	+247
	b_2 = 14·66	+0·666	+0·604	+0·438	
	b_3 = 10·07	−0·407	−0·199	+0·892	
90°	b_1 = 11·16	+0·912	+0·411	0	−335
	b_2 = 13·57	−0·411	+0·912	0	
	b_3 = 13·51	0	0	+1	

Table 5 lists the polarisability semi-axes and molar Kerr constants calculated for conformations of benzamide defined by angles ϕ (where ϕ is the dihedral angle between the planes of the amide group and of the aromatic ring; *e.g.*, for a planar molecule, $\phi = 0°$). The permanent electric moment components in the X, Y, and Z directions (see Figure 1) are: $\mu_x = 3·76 \cos 40$; $\mu_y = 3·76 \sin 40$; $\mu_z = 0$. The observed molar Kerr constant (+234 × 10^{-12}) is lower than that calculated for the solid-state configuration ($\phi = 26°$ from an X-ray analysis by Penfold and White [18]) and corresponds to an angle ϕ of *ca.* 37°. The uncertainty in ϕ, though difficult to assess, may reasonably be taken as ±5°.

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* *I.e.*, the semi-axes of acetamide less three C–H bond contributions; the assumption here that $b_2 = b_3$ for the $H_2N·CO·C$ group should introduce no serious error in the estimates of $_{\rm m}K$ calc. (for benzamide) in the presence of the highly anisotropic phenyl group.

[18] B. R. Penfold and J. C. B. White, *Acta Cryst.*, 1959, **12**, 130.

NN-*Diphenylformamide*.—Polarisability parameters and molar Kerr constants computed for conformations of *NN*-diphenylformamide are given in Table 6. The polarisabilities of the $C_2N{\cdot}CO{\cdot}H$ group were taken as $b_1 = 5{\cdot}22$, $b_2 = b_3 = 2{\cdot}76$, *i.e.*, the semi-axes of *NN*-dimethylformamide (assuming axial symmetry) less six C–H link contributions. The electric moment components along the reference axes X, Y, Z, were calculated on the basis that μ(*NN*-diphenylformamide) is resolvable into μ_a and μ_b, where μ_a is equivalent to the moment of *NN*-dimethylformamide and μ_b is the vector sum of mesomeric moments directed along each $\overset{+\!\!\!\rightarrow}{\mathrm{N{-}C_{Ar}}}$ axis. From μ(resultant) $= 3{\cdot}44$ D and $\mu_a = 3{\cdot}91$ D, the magnitude of μ_b follows as $0{\cdot}6_5$ D and the location of μ(resultant) as 47° from the X direction (see Figure 2). The calculated molecular refraction obtained[19] as R(*NN*-dimethylformamide) + $2R(C_6H_6) - 8R$(C–H) is 1·1 c.c. smaller than the observed value, and this corresponds to a polarisability exaltation (Δb) of 1·24 Å.[3] In the calculations we assign an increment of polarisability ($\Delta b/2$) as operative along each phenyl 1,4-axis. Conformations of *NN*-diphenylformamide are defined, in Table 6, by (equal) angles of rotation (α°) of the phenyl groups, in the same sense from a theoretical planar model for which $\alpha = 0°$. The observed molar Kerr constant (406×10^{-12}) is in closest agreement with that calculated for $\alpha = 52°$ ($\pm 5°$).

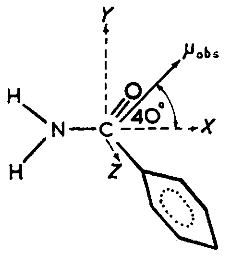

FIGURE 1

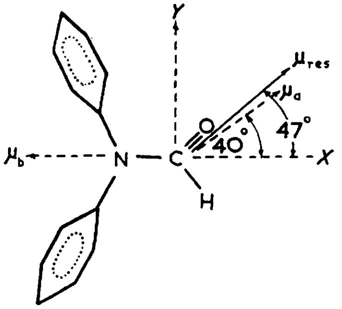

FIGURE 2

TABLE 6

Polarisabilities and molar Kerr constants calculated for conformations of *NN*-diphenylformamide

α	b_i (calc.)	Direction cosines with X	Y	Z	$10^{12}{}_mK$ (calc.)
0°	$b_1 = 24{\cdot}54$	+0·723	−0·691	0	904
	$b_2 = 26{\cdot}93$	+0·691	+0·723	0	
	$b_3 = 16{\cdot}20$	0	0	+1	
52°	$b_1 = 21{\cdot}88$	+0·922	−0·170	−0·348	409 *
	$b_2 = 25{\cdot}72$	+0·295	+0·889	(+) +0·349	
	$b_3 = 20{\cdot}06$	+0·251 (−)	−0·424 (+)	(−) +0·870	
90°	$b_1 = 19{\cdot}60$	+0·965	−0·264	0	113
	$b_2 = 24{\cdot}19$	+0·264	+0·965	0	
	$b_3 = 23{\cdot}88$	0	0	+1	

* The signs in parentheses refer to rotations of the phenyl groups in the anti-clockwise direction with respect to the X axis in Figure 2.

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