

sponding to the third row and column of S are zero. According to our second law, it will be: $T_{12} = L_{12} = 0$, and $T_{11} = T_{22}$; $L_{11} = L_{22}$. From (9), since $g = 2$ and $h = 4$, we also have: $T_{11} = 2(T_{1(11)} \pm T_{1(22)}) = T_{22}$, and similarly for $L_{11} = L_{22}$. This is in agreement with our results (Filippini, Gramaccioli, Simonetta & Suffritti, 1976a) and with ST.

References

- BONADEO, H. & BURGOS, E. (1982). *Acta Cryst.* **A38**, 29–33.
 BONADEO, H. & TADDEI, G. (1973). *J. Chem. Phys.* **58**, 979–984.
 COCHRAN, W. & PAWLEY, G. S. (1964). *Proc. R. Soc. London Ser. A*, **280**, 1–22.
 CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 747–753, 754–756, 757–758.
 FILIPPINI, G., GRAMACCIOLI, C. M., SIMONETTA, M. & SUFFRITTI, G. B. (1973). *J. Chem. Phys.* **59**, 5088–5101.
 FILIPPINI, G., GRAMACCIOLI, C. M., SIMONETTA, M. & SUFFRITTI, G. B. (1974a). *Acta Cryst.* **A30**, 189–196.
 FILIPPINI, G., GRAMACCIOLI, C. M., SIMONETTA, M. & SUFFRITTI, G. B. (1974b). *Chem. Phys. Lett.* **26**, 301–304.
 FILIPPINI, G., GRAMACCIOLI, C. M., SIMONETTA, M. & SUFFRITTI, G. B. (1976a). *Acta Cryst.* **A32**, 259–264.
 FILIPPINI, G., GRAMACCIOLI, C. M., SIMONETTA, M. & SUFFRITTI, G. B. (1976b). *Chem. Phys. Lett.* **39**, 14–18.
 FILIPPINI, G., GRAMACCIOLI, C. M., SIMONETTA, M. & SUFFRITTI, G. B. (1978). *Mol. Phys.* **35**, 1659–1667.
 GRAMACCIOLI, C. M. & FILIPPINI, G. (1983). *Acta Cryst.* **A39**, 784–791.
 GRAMACCIOLI, C. M. & FILIPPINI, G. (1984). *Chem. Phys. Lett.* **108**, 585–588.
 GRAMACCIOLI, C. M. & FILIPPINI, G. (1985). *Acta Cryst.* **A41**, 361–365.
 GRAMACCIOLI, C. M., FILIPPINI, G. & SIMONETTA, M. (1982). *Acta Cryst.* **A38**, 350–356.
 GWINN, W. D. (1971). *J. Chem. Phys.* **55**, 477–481.
 JOHNSON, C. K. (1970). In *Crystallographic Computing*, edited by F. R. AHMED, pp. 207–226. Copenhagen: Munksgaard.
 JOHNSON, C. K. (1980). In *Computing in Crystallography*, edited by R. DIAMOND, S. RAMASESHAN & K. VENKATESAN, pp. 14.01–14.85. Bangalore: The Indian Academy of Sciences.
 KROON, P. A. & VOS, A. (1979). *Acta Cryst.* **A35**, 675–684.
 NETO, N., RIGHINI, R., CALIFANO, S. & WALMSLEY, S. H. (1978). *Chem. Phys.* **29**, 167–179.
 PAWLEY, G. S. (1967). *Phys. Status Solidi*, **30**, 347–360.
 PAWLEY, G. S. (1968). *Acta Cryst.* **B24**, 485–486.
 PAWLEY, G. S. (1972a). In *Advances in Structure Research by Diffraction Methods*, Vol. 4, edited by W. HOPPE & R. MASON, pp. 1–64. Oxford: Pergamon Press.
 PAWLEY, G. S. (1972b). *Phys. Status Solidi* **B49**, 475–488.
 PAWLEY, G. S. & RINALDI, R. P. (1972). *Acta Cryst.* **B28**, 3605–3609.
 SCHERINGER, C. (1972a). *Acta Cryst.* **A28**, 512–515.
 SCHERINGER, C. (1972b). *Acta Cryst.* **A28**, 516–522.
 SCHERINGER, C. (1972c). *Acta Cryst.* **A28**, 616–619.
 SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
 TADDEI, G., BONADEO, H., MARZOCCHI, M. P. & CALIFANO, S. (1973). *J. Chem. Phys.* **58**, 966–978.
 WILLIS, B. T. M. & HOWARD, J. A. K. (1975). *Acta Cryst.* **A31**, 514–520.
 WILLIS, B. T. M. & PRYOR, A. N. (1975). *Thermal Vibrations in Crystallography*. Cambridge Univ. Press.
 WILSON, E. B. JR., DECIUS, J. C. & CROSS, P. C. (1955). *Molecular Vibrations* pp. 22–25. New York: McGraw-Hill.

Acta Cryst. (1985). **A41**, 361–365

Thermal Motion Analysis in *o*-Terphenyl: a Lattice-Dynamical Approach

BY CARLO MARIA GRAMACCIOLI

Earth Science Department, University of Milan, Via Botticelli 23, I-20133 Milano, Italy

AND GIUSEPPE FILIPPINI

Department of Physical Chemistry and CNR Centre, University of Milan, Via Golgi 19, I-20133 Milano, Italy

(Received 15 September 1984; accepted 15 January 1985)

Abstract

A 'non-rigid' harmonic lattice-dynamical model has been used for calculating thermal motion in crystals of *o*-terphenyl. For this purpose, empirical internal and external force fields, derived from a series of other aromatic hydrocarbons have been employed. The agreement between calculated anisotropic temperature factors and corresponding neutron-diffraction data is excellent (10%); it becomes decidedly worse if intramolecular van der Waals interactions are neglected in our model. Bond-length corrections for the general case of non-rigid thermal motion are

made: the differences with respect to the 'ordinary' rigid-body model are particularly evident for the C–H bonds.

Introduction

The need to know thermal motion in crystals on a rational basis is rapidly developing nowadays. This may be essential for improving the empirical force fields, which too often do not distinguish between the free and the packed molecules. Other important applications are in electron density measurements, and even for establishing the mechanism of movement

for some molecules of biological origin (Frauenfelder, Petsko & Tsernoglou, 1979; Artymiuk, Blake, Grace, Oatley, Phillips & Sternberg, 1979), or the particular situation in some inorganic complexes, involving - for instance - the dynamic Jahn-Teller effect (Bürgi & Dunitz, 1983).

Until quite recently, most information of this kind came from measurements of anisotropic crystallographic temperature factors; other major sources of information are Raman or infrared spectroscopic measurements, with a few data coming from inelastic neutron scattering. However, relatively little has been done to correlate all these measurable quantities. Too often, in fact, temperature factors are only regarded as additional parameters for improving the fit to observed data in least-squares crystallographic measurements.

An independent way of checking such temperature factors comes from lattice-dynamical estimation. Such calculations have been avoided for a long time as quite forbidding. On the other hand, it has been shown that for the rigid body the harmonic approximation can reproduce the experimental values of the B 's quite well, even using simple van der Waals fields (Pawley, 1967; Filippini, Gramaccioli, Simonetta & Suffritti, 1973, 1974*a,b*, 1976*a,b*; Willis & Howard, 1975; Filippini, Gramaccioli & Simonetta, 1981; Gramaccioli, Filippini & Simonetta, 1982; Kroon & Vos, 1979); the sampling of the Brillouin zone can be reduced to a few hundreds of points if an unevenly spaced grid is adopted (Filippini, Gramaccioli, Simonetta & Suffritti, 1976*a*).

For non-rigid molecules, such procedures can be easily extended without increasing the computing time considerably (Gramaccioli & Filippini, 1983, here onwards referred to as GF; 1984*a,b*).

The agreement of the calculated B 's with the corresponding experimental values has always turned out to be good: on this basis, the calculated values for the coupling tensors $U(\kappa\kappa') = \langle \mathbf{u}(\kappa) | \mathbf{u}(\kappa') |^T \rangle$ between the displacements of different atoms κ and κ' can be expected to be reliable, although such data cannot be checked by comparison with X-ray diffraction measurements.

After having considered several aromatic hydrocarbons, from benzene to pyrene (see GF), we turned our attention to derivatives of diphenyl. For instance, diphenyl itself has been extensively studied from this point of view, and it was actually the first example of a lattice-dynamical calculation of this kind with a non-rigid molecular model (Bonadeo & Burgos, 1982). The only internal degree of freedom considered by these authors was the rotation of the phenyl rings around the central C—C bond; however, a possible extensive rocking of such rings around this bond cannot indeed be excluded.

For more complex molecules of this kind, rigidity becomes less and less justified, and even a model

accounting for rotation around the C—C bonds joining the phenyl rings may not be adequate. For testing such effects, an excellent example of a complex molecule related to diphenyl is *o*-terphenyl, of which an accurate neutron diffraction study has been performed (Brown & Levy, 1979).

At room temperature, the structure of the crystalline phase of *o*-terphenyl with $P2_12_12_1$ symmetry is completely ordered, unlike those of other terphenyl isomers, and no extensive anharmonic effects are expected to occur.

Method of calculation

Our procedure of calculation has been reported in GF, and details about the Brillouin-zone sampling are given by Filippini, Gramaccioli, Simonetta & Suffritti (1976*a*).^{*} The van der Waals field is given by Williams (1967), and a maximum interaction distance of 5.5 Å is assumed. The internal force field for 'in-plane' movements in the aromatic rings is the one proposed by Neto, Scrocco & Califano (1966: here onwards NSC), and for 'out-of-plane' movements the force field proposed by Filippini, Simonetta & Gramaccioli (1984: here onwards FSG) was used; the torsional force constants around the inter-ring bonds are assumed to be zero. Such force fields give a satisfactory agreement with the measured vibration frequencies in crystals of several aromatic hydrocarbons.

Another field, which was specifically proposed for interpreting the 'in-plane' vibrations of diphenyl, is given by Zerbi & Sandroni (1968; here onwards ZS). However, this field cannot be applied as such to terphenyl, since the diphenyl molecule is planar in the crystal, unlike the terphenyl molecule. For this reason, owing to the different geometry, the van der Waals internal repulsion effects are quite strong and completely different in the two cases: such effects were implicitly accounted for in deriving ZS's force-field constants.

A comparison of the empirical constants assumed by NSC and ZS shows considerable similarity between the two fields, the major differences being in some interaction constants involving the atoms at the link between the two phenyls. These constants, however, are the ones that are most directly influenced by the internal van der Waals repulsion.

Calculation of vibrational frequencies in crystalline diphenyl using NSC and FSG force constants, including internal van der Waals interactions, shows essential agreement with the experimental data. The only exception seems to be a frequency ($\nu_{10}B_{2u}$), which

^{*} In our opinion, more elaborate schemes of Brillouin-zone sampling (see, for instance, Kroon & Vos, 1978, 1979) do not seem to offer any advantage upon our sampling, at least for these purposes.

Table 1. *The tensor W for o-terphenyl (atomic mass units $\times \text{Å}^2$; referred to the principal axes of inertia: see GF)*

The rows and columns refer, in sequence, to translational, rotational and internal coordinates in order of increasing frequency (cm^{-1}) in the isolated molecule. The conformation of the isolated molecule is assumed to be the same as in the crystal.

Translational			Rotational			Internal modes					
q_1	q_2	q_3	q_4	q_5	q_6	$q_7(56\cdot1)$	$q_8(58\cdot1)$	$q_9(68\cdot6)$	$q_{10}(102\cdot1)$	$q_{11}(115\cdot9)$	$q_{12}(153\cdot1)$
9.549	0.543	-0.702	-0.626	1.627	-2.107	-0.130	-0.026	-0.166	-0.095	-0.128	0.032
	9.466	-0.363	0.268	0.123	0.105	-0.060	-0.045	-0.154	0.179	0.061	-0.025
		9.778	-2.246	1.478	0.593	0.255	0.149	0.213	-0.006	0.114	0.011
			4.813	-1.772	-0.033	-0.233	0.363	0.219	-0.101	-0.103	-0.016
				4.187	-1.071	0.333	0.053	-0.241	0.216	-0.044	0.049
					5.236	0.159	-0.727	0.561	-0.044	0.197	0.008
						1.020	0.040	0.010	0.046	-0.013	0.005
							1.301	-0.004	0.003	-0.051	-0.036
								0.937	-0.043	0.006	-0.019
									0.540	0.001	0.007
										0.428	0.000
											0.281

becomes much higher ($198\text{--}200\text{ cm}^{-1}$) than the reported experimental value (116 cm^{-1}) if the internal van der Waals interactions are included in the calculations. This happens because of the considerable repulsion between adjacent atoms belonging to different phenyl rings. However, according to ZS, the attribution of this frequency is uncertain, and in our opinion it might well be a lattice mode. Since the *o*-terphenyl molecule is bent, such a problem does not arise in our calculations for this substance.

Therefore, in spite of virtual lack of spectroscopic measurements [no data are reported below 500 cm^{-1} in the only work on this subject, due to Sandroni & Geiss (1966)], we are substantially confident about the essential transferability for our purposes of NSC and FSG fields to terphenyl. For the sake of clarity, the **F** matrix including all force constants (and interaction constants) is given in Table 1*a*.*

As we showed in GF, our calculations in the crystal include a certain number of internal degrees of freedom in the dynamical matrices, corresponding to the normal coordinates of the free molecule whose frequencies are below a certain value (here 200 cm^{-1}). In this case, such a limit corresponds to including six internal degrees of freedom to mix with the lattice modes; the contribution of higher-frequency modes has been added as for the free molecule (see GF, and Gramaccioli, Filippini & Simonetta, 1982). The lattice modes of the crystal, calculated on this basis (below 200 cm^{-1}) at the Γ point ($\mathbf{k}=0$) are reported in Table 2*a*, and the first 12×12 block of the mean-square displacement tensor **W** is reported in Table 1; the relationship of such tensors to the molecular vibration tensors **T**, **L**, **S** of Schomaker & Trueblood (1968) is given in GF. Values of **T**, **L**, **S** tensors for *o*-terphenyl,

Table 2. *Rigid-body vibrational tensors T, L and S ($\times 10^4$) for the o-terphenyl molecule (in Å^2 , rad^2 , Å rad , respectively) (1) from our lattice-dynamical calculations; (2) from the Schomaker-Trueblood fit to temperature factors*

The reference system is Cartesian, where *x*, *y* and *z* coincide in direction with the crystallographic axes *a*, *b* and *c*, respectively.

	T			L			S		
(1)	400	-14	7	34	-14	-3	1	-21	20
		462	1		30	9	1	29	-17
			389			48	50	2	-25
(2)	427	-54	22	46	-15	-1	1	-12	9
		452	70		46	16	10	28	-37
			543			77	51	3	-29

as evaluated through **W**, are reported in Table 2, together with the corresponding values of such tensors, as derived from a 'usual' ST fit to experimental temperature factors.

Results and discussion

The calculated values of anisotropic temperature factors (**B**'s) are reported in Table 3, together with the corresponding observed values (Brown & Levy, 1979). The reported σ 's for diagonal elements of the **B**'s are about 3% for C atoms and 6% for H atoms. The disagreement indices between observed and calculated values of the **B**'s, $R = \sum |B_{ij(\text{obs})} - B_{ij(\text{calc})}| / \sum B_{ij(\text{obs})}$, and $\Delta B = \sum (B_{ij(\text{obs})} - B_{ij(\text{calc})}) / \sum B_{ij(\text{obs})}$ are 10.2 and 2.1%, respectively. Since the two ways of deriving the B_{ij} 's are completely independent, and considering the possible influence of various systematic errors, the agreement is indeed remarkable.

On these grounds, the effect of systematic errors due to thermal diffuse scattering, or absorption, etc. are not particularly evident. A similar case has been encountered for pyrene (see GF), where accurate collecting by neutron diffraction, with cutoff of low-angle reflections, and choice of an appropriate data-

* Tables 1*a*-2*a* have been deposited with the British Library Lending Division as Supplementary Publications No. SUP 39979 (5 pp.) Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Temperature factors for o-terphenyl* ($\text{\AA}^2 \times 10^4$)

They are in the form $t_i = \exp[-B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl]$. The first line, for each atom, refers to calculated values; the second line refers to the corresponding observed value by Brown & Levy (1979).*

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1) (cal)	33	290	65	-11	-1	-1
(obs)	30	277	55	-10	-2	4
C(2) (cal)	32	350	84	2	6	-20
(obs)	28	324	78	-1	2	-20
C(3) (cal)	44	458	99	32	10	-35
(obs)	40	449	90	35	8	-28
C(4) (cal)	69	404	98	45	4	-41
(obs)	67	354	98	45	-4	-46
C(5) (cal)	74	307	97	-1	-5	-29
(obs)	70	291	99	-4	-9	-25
C(6) (cal)	51	303	80	-27	-5	-2
(obs)	48	323	82	-33	-7	0
C(1') (cal)	24	326	66	-13	-1	4
(obs)	24	333	60	-12	1	8
C(2') (cal)	23	313	69	-1	0	-4
(obs)	22	327	58	-6	1	3
C(3') (cal)	26	387	80	13	3	-10
(obs)	30	398	73	28	7	14
C(4') (cal)	25	513	92	24	4	6
(obs)	28	566	93	36	9	15
C(5') (cal)	23	583	92	5	-2	16
(obs)	22	642	100	18	-1	26
C(6') (cal)	25	467	77	-17	-4	9
(obs)	23	529	79	-11	-2	1
C(1'') (cal)	25	333	76	7	-3	-28
(obs)	25	301	67	10	-4	-26
C(2'') (cal)	25	399	120	-5	-1	-63
(obs)	29	343	118	-11	-1	-48
C(3'') (cal)	25	618	161	4	-10	-136
(obs)	29	595	162	-14	-8	-132
C(4'') (cal)	32	760	139	59	-25	-142
(obs)	35	752	138	62	-27	-135
C(5'') (cal)	46	598	105	74	-23	-54
(obs)	49	592	112	75	-24	-37
C(6'') (cal)	38	395	83	29	-10	-15
(obs)	38	356	86	21	-12	-1
H(2) (cal)	36	469	139	-24	9	-48
(obs)	37	432	161	-25	14	-93
H(3) (cal)	52	722	171	33	23	-55
(obs)	43	743	171	39	23	-68
H(4) (cal)	101	625	158	81	6	-76
(obs)	94	621	161	95	12	-102
H(5) (cal)	111	403	172	-30	-10	-71
(obs)	124	404	175	-56	-19	-66
H(6) (cal)	67	438	137	-71	-4	5
(obs)	56	529	163	-96	4	-1
H(3') (cal)	37	539	116	22	-1	-44
(obs)	46	493	123	38	1	-72
H(4') (cal)	39	758	132	55	3	-6
(obs)	45	803	148	97	10	0
H(5') (cal)	31	924	137	12	-7	16
(obs)	28	1017	175	17	-10	2
H(6') (cal)	36	676	110	-30	-14	-9
(obs)	37	786	118	-35	-19	-23
H(2'') (cal)	44	439	182	-26	7	-41
(obs)	48	381	218	-8	-3	16
H(3'') (cal)	39	820	278	-44	-9	-186
(obs)	39	893	292	-69	-19	-185
H(4'') (cal)	47	1158	214	81	-39	-199
(obs)	41	1203	245	81	-50	-185
H(5'') (cal)	82	796	159	113	-35	-22
(obs)	82	711	183	99	-38	60
H(6'') (cal)	62	422	136	2	-9	26
(obs)	63	407	161	-9	-20	56

* The unit-cell parameters are: $a = 18.583$; $b = 6.024$; $c = 11.728$ \AA; $\alpha = \beta = \gamma = 90^\circ$.

collection strategy (Hazell, Larsen & Lehmann, 1972) resulted in a very good agreement with the result of lattice-dynamical calculations.

Table 4. *Bond distances* (\AA) in *o-terphenyl*, uncorrected and corrected for 'rigid' or 'non-rigid' thermal motion (in sequence)

Labelling for the atoms is the same as in Brown & Levy (1979), from which the uncorrected values have been taken.

C(1)-C(2)	1.400	1.409	1.413	C(1)-C(6)	1.394	1.402	1.407
C(1)-C(1')	1.492	1.499	1.501	C(2)-C(3)	1.393	1.399	1.405
C(2)-H(2)	1.080	1.087	1.104	C(3)-C(4)	1.382	1.390	1.396
C(3)-H(3)	1.083	1.090	1.109	C(4)-C(5)	1.387	1.396	1.401
C(4)-H(4)	1.117	1.122	1.141	C(5)-C(6)	1.379	1.385	1.390
C(5)-H(5)	1.085	1.091	1.110	C(6)-H(6)	1.105	1.112	1.129
C(1')-C(2')	1.403	1.409	1.411	C(1')-C(6')	1.401	1.410	1.411
C(2')-C(3')	1.403	1.410	1.412	C(2')-C(1'')	1.481	1.490	1.491
C(3')-C(4')	1.386	1.395	1.397	C(3')-H(3')	1.080	1.085	1.102
C(4')-C(5')	1.387	1.394	1.398	C(4')-H(4')	1.076	1.081	1.098
C(5')-C(6')	1.384	1.391	1.394	C(5')-H(5')	1.096	1.103	1.119
C(6')-H(6')	1.103	1.109	1.125	C(1'')-C(2'')	1.386	1.396	1.401
C(1'')-C(6'')	1.383	1.392	1.398	C(2'')-C(3'')	1.389	1.397	1.402
C(2'')-H(2'')	1.087	1.094	1.112	C(3'')-C(4'')	1.373	1.382	1.389
C(3'')-H(3'')	1.089	1.096	1.116	C(4'')-C(5'')	1.394	1.404	1.410
C(4'')-H(4'')	1.084	1.090	1.109	C(5'')-C(6'')	1.393	1.401	1.406
C(5'')-H(5'')	1.090	1.097	1.117	C(6'')-H(6'')	1.086	1.093	1.112

From inspection of the mean-square displacement tensor W , it can be observed that even in this case thermal motion does not deviate considerably from the rigid-body behaviour, since the highest elements are in the first six rows and columns; however, a few cross terms between internal and external modes are not particularly small. If the values of T , L and S that are reported in the first row of Table 2 (*i.e.* the lattice-dynamical estimation of such quantities) are used for calculating the B 's without any internal-mode contribution, the disagreement index R is 22.9%.

Such 'quasi-rigid' behaviour is very probably due to the 'packed up' nature of the molecule, with strong internal van der Waals interactions. This is suggested by the closeness of atoms in different rings, and also by the significant distortion at the ends of inter-ring bonds (Brown & Levy, 1979). If such internal van der Waals contributions to the force field are omitted from our calculations, the disagreement index relative to the B 's raises to 30%.

In line with these observations, the ST fit to temperature factors gives a good agreement ($R = 13.2\%$) with a rigid-body model, and the corresponding values of T , L and S show essential agreement with the 'lattice dynamical' estimates (see Table 2). On the whole, however, the 'rigid body' values are somewhat higher than the 'lattice dynamical' values. This can be easily explained, since in the ST fit the contribution of internal modes is forced to be interpreted as a rigid-body libration and translation. Such differences are not negligible when bond-length corrections are calculated: in Table 4, these corrections have been derived from the L tensor in the ST fit (column 2), or for non-rigid libration (column 3). In the latter case, the procedure mentioned by Scheringer (1972) or Johnson (1980) has been used, and for this purpose the coupling tensors $U(\kappa\kappa')$ between different atoms have been evaluated through lattice dynamics, as we showed in GF.

In summary, we have shown that for complex polyphenyl molecules temperature factors and bond-length corrections can be calculated without extensive difficulty, using transferable force fields, as derived from a group of similar substances. Such temperature factors seem to agree very well with good experimental measurements and with other conformational data derived from solution of crystal structures. The computing time, for the whole procedure, is about 50 min on a machine like Siemens 7.865, using our set of programs (Gramaccioli & Filippini, 1985).

We thank Dr Tullio Pilati for helpful proposals and discussions.

References

- ARTYMIUK, P. J., BLAKE, C. C. F., GRACE, D. E. P., OATLEY, S. J., PHILLIPS, D. C. & STERNBERG, M. J. E. (1979). *Nature (London)*, **280**, 563-568.
- BONADEO, H. & BURGOS, E. (1982). *Acta Cryst.* **A38**, 29-33.
- BROWN, G. M. & LEVY, H. A. (1979). *Acta Cryst.* **B35**, 785-788.
- BÜRGI, H. B. & DUNITZ, J. D. (1983). *Acc. Chem. Res.* **16**, 153-161.
- FILIPPINI, G., GRAMACCIOLI, C. M. & SIMONETTA, M. (1981). *Chem. Phys. Lett.* **79**, 470-475.
- FILIPPINI, G., GRAMACCIOLI, C. M., SIMONETTA, M. & SUFRITTI, G. B. (1973). *J. Chem. Phys.* **59**, 5088-5101.
- FILIPPINI, G., GRAMACCIOLI, C. M., SIMONETTA, M. & SUFRITTI, G. B. (1974a). *Acta Cryst.* **A30**, 189-196.
- FILIPPINI, G., GRAMACCIOLI, C. M., SIMONETTA, M. & SUFRITTI, G. B. (1974b). *Chem. Phys. Lett.* **26**, 301-304.
- FILIPPINI, G., GRAMACCIOLI, C. M., SIMONETTA, M. & SUFRITTI, G. B. (1976a). *Acta Cryst.* **A32**, 259-264.
- FILIPPINI, G., GRAMACCIOLI, C. M., SIMONETTA, M. & SUFRITTI, G. B. (1976b). *Chem. Phys. Lett.* **39**, 14-18.
- FILIPPINI, G., SIMONETTA, M. & GRAMACCIOLI, C. M. (1984). *Mol. Phys.* **51**, 445-449.
- FRAUENFELDER, H., PETSCH, G. A. & TSEBNOGLOU, D. (1979). *Nature (London)*, **280**, 558-563.
- GRAMACCIOLI, C. M. & FILIPPINI, G. (1983). *Acta Cryst.* **A39**, 784-791.
- GRAMACCIOLI, C. M. & FILIPPINI, G. (1984a). *Chem. Phys. Lett.* **104**, 50.
- GRAMACCIOLI, C. M. & FILIPPINI, G. (1984b). *Chem. Phys. Lett.* **108**, 585.
- GRAMACCIOLI, C. M. & FILIPPINI, G. (1985). *Acta Cryst.* **A41**, 356-361.
- GRAMACCIOLI, C. M., FILIPPINI, G. & SIMONETTA, M. (1982). *Acta Cryst.* **A38**, 350-356.
- HAZELL, A. C., LARSEN, F. K. & LEHMANN, M. S. (1972). *Acta Cryst.* **B28**, 2977-2984.
- JOHNSON, C. K. (1980). In *Computing in Crystallography*, edited by R. DIAMOND, S. RAMASESHAN & K. VENKATESAN, pp. 14.01-14.15. Bangalore: Indian Academy of Sciences.
- KROON, P. A. & VOS, A. (1978). *Acta Cryst.* **A34**, 823-824.
- KROON, P. A. & VOS, A. (1979). *Acta Cryst.* **A35**, 675-684.
- NETO, N., SCROCCO, M. & CALIFANO, S. (1966). *Spectrochim. Acta*, **22**, 1981-1998.
- PAWLEY, G. S. (1967). *Phys. Status Solidi*, **20**, 347-360.
- SANDRONI, S. & GEISS, F. (1966). *Z. Anal. Chem.* **220**, 321-333.
- SCHERINGER, C. (1972). *Acta Cryst.* **A28**, 616-619.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63-76.
- WILLIAMS, D. E. (1967). *J. Chem. Phys.* **47**, 4680-4684.
- WILLIS, B. T. M. & HOWARD, J. A. K. (1975). *Acta Cryst.* **A31**, 514-520.
- ZERBI, G. & SANDRONI, S. (1968). *Spectrochim. Acta Part A*, **24**, 483-510, 511-528.

Acta Cryst. (1985). **A41**, 365-371

X-ray Dichroism and Anomalous Scattering of Potassium Tetrachloroplatinate(II)

BY DAVID H. TEMPLETON AND LIESELOTTE K. TEMPLETON

*Materials and Molecular Research Division, Lawrence Berkeley Laboratory and
Department of Chemistry, University of California, Berkeley, California 94720, USA*

(Received 16 November 1984; accepted 15 January 1985)

Abstract

X-ray dichroism is observed at the *L* absorption edges of Pt in K_2PtCl_4 , and the anomalous scattering tensor for Pt in this square-planar complex is measured in experiments with linearly polarized synchrotron radiation. For special azimuthal settings the diffraction intensities of some reflections depend on only one or the other of the principal values of the tensor. The polarization anisotropy, which is as much as 10 electrons atom⁻¹ for f'' , is the largest yet reported for anomalous scattering. These phenomena offer a new way to determine diffraction phases, but add complications for previous methods using multiple wavelengths.

1. Introduction

Strong X-ray dichroism can occur near an absorption edge when the absorbing atom is in a suitable molecular environment. We are interested in the polarization anisotropy of the anomalous scattering, which is another aspect of this phenomenon, and in its consequences in diffraction experiments. The tensor that describes this anomalous scattering has already been measured in diffraction experiments with the linear uranyl (UO_2^{2-}) ion (Templeton & Templeton, 1982) and the pyramidal bromate (BrO_3^-) ion (Templeton & Templeton, 1985). In both cases cubic crystals were used to avoid some of the complications that these effects introduce into the diffraction